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A Method of Predicting the Thermal Conductivity of Some Hydrogen Bonded Binary Solutions That Form Bimolecular Complexes.

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ABSTRACT

The thermal conductivity of most binary solutions tends to be less than the mole fraction average of the pure components. This deviation tends to be more pronounced for highly non-ideal solutions particularly where hydrogen bonds are formed and/or broken upon mixing the pure components.

The formation of hydrogen bonds can be divided into three geometric groups:

1. Bimolecular complexes
2. Linear chains
3. Complicated three dimensional networks.

This work deals with binary solutions where the hydrogen bonds formed are of the first type-bimolecular complexes. The excess thermal conductivity or the deviation of the thermal conductivity from ideality is written in terms of a third order Hermite interpolating polynomial which requires a value of the slope of the excess thermal conductivity function at both ends of the composition range. These slopes were evaluated by assuming the binary solution formed by mixing the pure components is a chemically reacting ternary mixture in chemical equilibrium consisting of both the binary components plus the bimolecular hydrogen bonded complex. The resulting ternary mixture is assumed to form an ideal associated solution. In deriving an expression for the slope of the excess thermal conductivity function at both ends of the composition range, the contribution to the thermal

conductivity from the migration of the reacting species is evaluated using Fick's Law and the conduction contribution to thermal conductivity is evaluated from the thermal conductivity of the pure components and an estimated value of the thermal conductivity of the complex. The thermal conductivity of the complex is evaluated by treating the complex as a solute molecule whose mass and volume have been increased. This treats the complex as being formed by a structural addition to the solute molecule. The resulting equation for predicting the excess thermal conductivity requires the following data: thermal conductivity of the pure components, density, molecular weights, heat of reaction and an equilibrium constant for the formation of the hydrogen bonded complex, and mutual diffusion coefficients at infinite dilution.

The thermal conductivity measurements were made with a parallel plate apparatus which has been thoroughly tested. This apparatus has an accuracy of ±1.5% which includes a 1% consistent error in the thermal conductivity of the steel in the plates. The precision of the apparatus has been found to be ±0.23% at the 99.5% confidence level. Thermal conductivity measurements were made over the entire concentration range for six systems that form bimolecular complexes. Literature data was used for three other systems.

The agreement of calculated excess thermal conductivity with the experimental value was within 25%. Enough data was obtainable to permit a check of the derived equation with experiment without fitting any of the variables for seven of the nine binary systems.

For the remaining two systems, equilibrium constants were not obtainable and were fit to the experimental excess thermal conductivity. The resulting values of equilibrium constants were reasonable.

It was also concluded from the experimental data that increasing steric interference around the hydrogen bonding sites decreases the deviation from ideality of thermal conductivity. Previous work on alcohol-inert solvent systems shows the same effect.

Dedicated to the memory

of my mother and father.

CHAPTER 1
INTRODUCTION

Thermal conductivity, coefficient of shear viscosity, and the coefficient of diffusion are defined as constants of proportionality between flux and driving force. In the case of thermal conductivity, the flux is heat and the driving force is the gradient of temperature.

An approximation to the thermal conductivity of binary solutions might be to take the thermal conductivity of a binary solution as a mole fraction average of the pure component thermal conductivities. In reality, it is known that the thermal conductivity of a real binary solution is usually less than the mole fraction average.[1] As one would suspect, as the solution approaches ideality, the difference in the mole fraction average thermal conductivity and the real thermal conductivity approaches zero. This can readily be seen by observing the thermal conductivity data for benzene-toluene.[2]

Solutions whose components form or break hydrogen bonds tend to be highly non-ideal.[3] As one would suspect, the thermal conductivities of these solutions are also highly non-ideal. Prigogine and others[3,4,5,7,8,10,11,12] have approached the problem of predicting thermodynamic properties of hydrogen bonded binary solutions by treating a binary solution as an equilibrium mixture of binary components and hydrogen bonded complexes. This equilibrium mixture is then considered ideal and is called an ideal associated solution. This implies that differences in sizes between the complex and binary

components will be neglected and that the heat of solution is to be interpreted as the heat of reaction for the formation of the hydrogen bonded complex. Equations are then derived for thermodynamic properties in terms of hydrogen bond energies and an equilibrium constant for formation of complex from binary components. Both of these quantities can be evaluated by several independent means. In this treatment, the hydrogen bonded complex is considered a separate, distinct molecular specie. Therefore the hydrogen bond is thought of as a weak chemical bond. There is a wide variety of evidence which will be discussed in chapter three to indicate that treating the hydrogen bonded complex as a distinct molecular specie is reasonable. The same approach has been used to predict colligative properties of hydrogen bonded solutions.[6,9]

Barnette and Coates[13] have developed a method for predicting the excess thermal conductivity of alcohols dissolved in inert solvents. In these types of solutions the nonideality of the solution is considered to arise from breaking of hydrogen bonds between alcohol molecules. The solvent is considered to be non-hydrogen bonded or inert.

In Chapter 3 a method is developed for predicting the thermal conductivity of solutions where both of the components are reactive, that is, where the binary components react with each other to form a third component--a hydrogen bonded complex. The resulting solution of binary components and complex is assumed to form an ideal associated solution. An expression is then derived for the

excess thermal conductivity in terms of hydrogen bond energies, an equilibrium constant, diffusion coefficients at infinite dilution, and other properties of the pure components.

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CHAPTER 2
REVIEW OF PREVIOUS WORK

A. Pure Liquids

Sakiadis and Coates[1,2] have approached the prediction of thermal conductivity of pure liquids by treating heat conduction as the transfer of energy across isothermal molecular chains at sonic velocity. This takes the form of the Kardos equation $k = C_p \rho U L$ where k is the thermal conductivity, C_p is the heat capacity, ρ is the density, U is sonic velocity, and L the distance between the surfaces of the molecules. All quantities in this equation can be measured experimentally except L. The L term is evaluated from X-ray diffraction and critical density data or from structural considerations. This method when tested with experimental data, predicts the thermal conductivity of 42 liquids with an average deviation of ±2.6%.

Bridgman's equation[3] relates the thermal conductivity of a liquid with sonic velocity, the distance between molecular centers, and Boltzmann's constant. The result is $k = n\aleph U/l^2$ where n is a parameter (2), $\aleph$ is Boltzmann's constant, U is the velocity of sound, and l is the distance between molecular centers. When compared with experimental data the average deviation is about 10%.[23]

Viswanath[4] has modified Brigman's equation by substituting a relation for sonic velocity based on the hole theory of liquids and the Watson relation for the heat of vaporization. An average absolute

deviation of 9.5% is claimed for 16 liquids over the temperature range -20°C to +80°C and 5% for fifty liquids at 20°C.

Some work has been done on predicting thermal conductivity of simple spherically symetric molecules where the intermolecular potential can be expressed as a hard sphere, square well, or Leonard-Jones 12-6 potential.[23,24] The resulting expressions for thermal conductivity are generally quite complex and the deviation from the experimental values are often as high as 100%.

B. Binary Solutions

The thermal conductivity of real solutions is always less than the ideal thermal conductivity or the mole fraction average of the pure components.[13]

Using an analogy for estimating the viscosity of binary solutions[5], Jordan and Coates[6] have derived a similar expression for thermal conductivity. The result is $\ln k_m = w_1 \ln k_1 + w_2 \ln k_2 + w_1 w_2 \ln D$ where $D = e^{k_2 k_1 - \frac{(k_2+k_1)}{2}}$. The w's are weight fractions and k_1 and k_2 are pure component thermal conductivities. This method predicted the thermal conductivity of 12 binary organic mixtures to within ±2% and 9 binary water-organic mixtures within ±3%.

Rodriguez and Coates[25] have developed a means of using the Kardos equation for binary mixtures. In this approach, excess Gibb's free energy data is used to evaluate the intermolecular distance term. When compared with experimental data the average error was ±4%.

Fillipov and Novoselova[7,25] have proposed an empirical relation of the form: $k = w_1 k_1 + w_2 k_2 - C\, w_1 w_2 \mid k_1 - k_2 \mid$ where w_1 and w_2

are weight fractions of components 1 and 2, and k_1 and k_2 are the thermal conductivity of pure components 1 and 2 respectively. With C = 0.72 the deviation from experimental data was 1-2% for binary mixtures both associated and nonassociated.[9]

Bondi[8] recommends an equation of the form $k = x_1k_1 + x_2k_2 - fbx_1x_2$ where $f = \left|\left(\frac{E_1^o}{M_1}\right)^{\frac{1}{2}} - \left(\frac{E_2^o}{M_2}\right)^{\frac{1}{2}}\right|$ and b is a constant depending upon the units of E^o- for E^o in cal/gm mole $b = 4.5 \times 10^{-5}$ and for E in ergons/mole $b = 7.0 \times 10^{-5}$. E^o is the standard energy of vaporization $E^o = \Delta H - RT$ when $V/V_w = 1.70$ where V = molal volume and V_w = Van der Waals volume cc/gm mole and M_1 and M_2 are molecular weights. Bondii gives a technique for estimating E^o from structural considerations.

Tsederberg[9] has outlined a set of empirical rules for calculating thermal conductivity of binary solutions. The thermal conductivity of the solution may be taken as $k = w_1k_1 + w_2k_2$ if both components of the solution are normal liquids with zero dipole moments or if one component is polar and the other is nonpolar and the ratio of molecular weights does not exceed 1.6. This rule can also be used if the components are polar but normal with ratio of molecular weights not exceeding 1.25. This rule can also be used if one component is associated and polar and the other component is nonpolar and has no dipole moment and the ratio of molecular weights does not exceed 1.7. The rule may be used for solutions of 2 polar liquids, one of which is associated and the second normal with the ratio of molecular weights not exceeding 1.9.

C. Reacting Mixtures

Barnette and Coates[10] have treated alcohol-inert solvent systems as an effective ternary system which consists of monomer alcohol in equilibrium with an average polymer alcohol. The inert solvent acts as a diluent. A non-equilibrium thermodynamic approach was used to describe the heat flux of this system. An equation was then obtained relating the excess thermal conductivity of the mixture to the hydrogen bond energy, the equilibrium constant for the reaction, stoichiometric coefficient, mutual diffusion coefficients, density, and activity coefficients.

The derived equation was checked with experimental data and found to be accurate within 1% over the entire concentration range. Where hydrogen bond energies were not available, the hydrogen bond energy was treated as a parameter and varied to fit the experimental data. The values of hydrogen bond energies obtained in this fashion are reasonable for alcohol systems.

Eigen[11] has treated water as a reacting mixture by considering water as an equilibrium mixture of monomers and polymers. In this treatment, the thermal conductivity of water is taken to be the sum of two terms; one term is the thermal conductivity of water if all polymeric species were evenly distributed throughout the liquid. The other term is the increase of thermal conductivity due to diffusion effects. Eigen evaluated the first term by considering water as an unassociated fluid and the second term by using the Eucken[26] model for water. The agreement of theory with experiment was quite good.

Tyrrell[12] has treated the thermal conductivity of a gas or liquid where there is chemical reaction of the form $A \rightarrow \alpha B$. The thermal conductivity is then shown to consist of two terms: a normal thermal conductivity that can be thought of as the thermal conductivity if there were no chemical reaction present and a second term that can be thought of as the chemical reaction contribution to thermal conductivity, that is, the increase in thermal conductivity as a result of the diffusion of reacting species. However, no attempt is made to check the resulting expression with experimental data.

Considerable work has been done in the last 10 years on the thermal conductivity of reacting gases. Generally, this work can be divided into two categories[13]: first where the chemical reaction is very fast and secondly where the chemical reaction is not fast enough for equilibrium to exist, but fast enough to significantly increase the thermal conductivity. Hirschfelder[14] has indicated that the approach used on reacting gases should be applicable to reacting liquids. The heat flux is written in the form $q = -k_f \frac{dT}{dz} + \sum_i \bar{H}_i N_i$ where k_f is the thermal conductivity if there were no chemical equilibrium, $\bar{H}_i$ is the partial molal enthalpy of component i, and N_i represents the flux of component i in the z direction.

For the equilibrium case, the second term is evaluated in terms of the heat of reaction and the multidiffusion coefficients. Hirschfelder[14] has used this approach in treating the system $O_2 \rightleftarrows 2O$. Schotte and Chakraborti[15] have studied the system $PCl_5 \rightleftarrows PCl_3 + Cl_2$. Krieve[16] has studied the system $N_2O_4 \rightleftarrows 2NO_2$.

For the case where chemical reaction is not rapid enough to maintain chemical equilibrium, the mathematics becomes very complex because of the non-linear nature of the reaction-rate expression. Sherwood and Reid[13] have indicated that usually a specific rate expression must be known before a solution is possible, but reasonable solutions are available for the general case when it is permissible to linearize the expression. Some of the references for the treatment of the non-equilibrium cases are: 17,18,19,20,21, and 22.

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CHAPTER 3
THEORY

A. The Nature and Types of Hydrogen Bonding

Pimentel and McClellan[1] have defined a hydrogen bond as a weak chemical bond formed by the attraction between two functional groups in the same or different molecules in which one group serves as a proton donor (an acidic group) and the other as an electron donor (a basic group). Ordinary chemical bonds have energies on the order of 10 to 100 kilocalories/gm. mole while hydrogen bonds have energies on the order of 1 to 10 kilocalories/gm. mole.

Although the hydrogen bond is primarily electrostatic,[2] the electrostatic energy for a hydrogen bond is larger than the electrostatic energy for a dipole-dipole interaction. Since the hydrogen atom has no closed inner electron shells and since the electron density around the hydrogen atom in a hydrogen bond is small because the proton is attached to or close to an electron withdrawing group, the exchange energy, which is repulsive, is small. Since the exchange repulsion is small, the two molecules sharing the proton can approach closely and give a large electrostatic energy of attraction.[22]

For example, compounds such as water, ammonia, or hydrogen fluoride, which have low molecular weights and whose dipole moments

are not particularly high i.e., 1.85, 1.48, and 1.91 debye units respectively, have rather high boiling points. Ethyl bromide has a dipole moment of 1.83, which is almost as large as that of water, and a molecular weight that is about six times as great as water. However, ethyl bromide boils at 38°C compared with 100°C for water. Sulfur dioxide with a dipole moment of 1.6 and a molecular weight of 64 boils at -10°C. The reason for this great difference in behavior of these compounds when compared with water is that the bare proton when attached to strongly negative atoms is so small it can approach very closely to a second atom coupling with its electrons to form a hydrogen bond.[3]

The dissociation energy for a hydrogen bond is much greater than the kinetic energy of the molecule i.e., the kinetic energy is $3/2KT$ or about 0.06×10^{-12} ergs or 0.58 kcal/gm. mole while hydrogen bond energies are about 1-10 kilocalories/gm. mole. Hence collisions are only rarely energetic enough to break the hydrogen bond.[4]

Formation of hydrogen bonds can be interpreted in terms of the Lewis acid-base concept. The hydrogen bond can be thought of as being produced by the reaction of a Lewis acid, which has an active hydrogen, with a Lewis base, which is a proton acceptor.

The formation of intermolecular hydrogen bonds, that is, where the hydrogen bond is formed between two different molecules, can be divided into three classes:[5]

1. A hydrogen bonded complex is formed from 2 different molecules. One type of molecule is strictly the Lewis base and the other is strictly the Lewis acid, that is, a molecule cannot have both acidic and basic sites.
2. A hydrogen bonded complex is formed from one or more types of molecules where each molecule has both single Lewis acid and base sites. This type of complex can be of the form of a dimer, linear chain, or cyclic structure. Examples of this type are primary alcohols, organic acids, amines, and nitriles.
3. A hydrogen bonded complex is formed from one or more types of molecules where each molecule can have more than one Lewis acid and base sites. This type of complex tends to be a complicated three dimensional network. Examples of this type are water and glycols.

Intramolecular hydrogen bonds are those where the hydrogen bonds are formed between groups within a single molecule.

X-ray, electron diffraction, and neutron diffraction studies have indicated that the distance and orientation of the two molecules connected by the hydrogen bond are fixed. For example Pauling and Brockway[6] using the electron diffraction methods have found that the acetic acid dimer in the vapor state has the following structure:

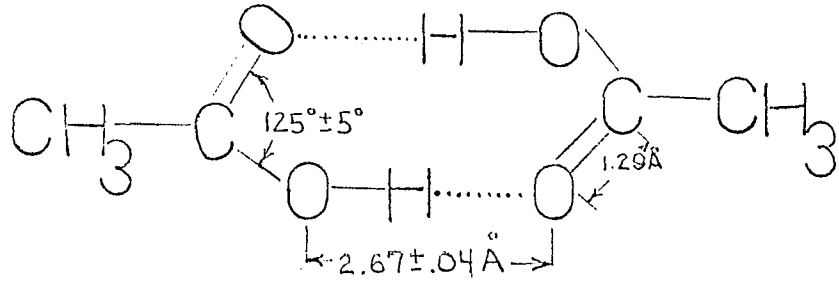

Figure 1 Structure of the Acetic Acid Dimer

Gulivets, Lutskii, and Radchenko[7] using X-ray diffraction methods report that liquid formic acid has a chain structure and liquid acetic acid has a cyclic dimer structure.

B. Diffusion and Conduction Contributions to Thermal Conductivity

Bird, Stewart, and Lightfoot[8] have written the energy flux of a mixture as the sum of the following terms:

$$\vec{e} = \vec{q}^{(c)} + \vec{q}^{(d)} + \vec{q}^{(x)} + \vec{q}^{(r)} \qquad (3\text{-}1)$$

where $\vec{q}^{(c)}$ is the conductive energy flux, $q^{(d)}$ is the energy flux arising from interdiffusion of the different species present, $\vec{q}^{(x)}$ is the Dufour energy flux which arises because of concentration gradients not associated with chemical reaction, and $\vec{q}^{(r)}$ is the radiant energy flux. For liquid systems, the Dufour energy flux is negligible and will not be considered. For liquids that are not strong absorbers of electromagnetic radiation and with a thin liquid layer, the radiant energy flux can be neglected. Therefore,

the energy flux consists of 2 terms: a conductive term and a diffusion term. The conductive contribution $\vec{q}^{(c)}$ is defined as:

$$\vec{q}^{(c)} = -k_f \bar{\nabla} T \tag{3-2}$$

and the diffusion term $\vec{q}^{(d)}$ is defined for an n specie fluid as:

$$\vec{q}^{(d)} = \sum_{i=1}^{n} \bar{H}_i \vec{N}_i \ , \tag{3-3}$$

where $\bar{H}_i$ is the partial molal enthalpy of component i and $\vec{N}_i$ is the molar flux of component i. The molal flux $\vec{N}_i$ can be expressed in terms of the definition of the effective binary diffusivity D_{im} with no bulk flow:

$$\vec{N}_i = -cD_{im} \bar{\nabla} x_i \tag{3-4}$$

where c is the total molar concentration and x_i is the mole fraction of component i.

The equation for the energy flux in the z direction in terms of an effective binary diffusivity can be written as:

$$e = - k_f \frac{\partial T}{\partial z} - \sum_{i=1}^{n} \bar{H}_i c \, D_{im} \frac{\partial x_i}{\partial z} \tag{3-5}$$

This equation as written assumes that the diffusion coefficients are the same for an isothermal as a non-isothermal system. This has been done in the case of gases. Some recent work[20] has indicated

that the non-isothermal diffusion coefficients are higher than the isothermal diffusion coefficients. However, enough work has not been done to justify any conclusions.

In section C of this chapter, some simplifying assumptions will be made for dealing with the diffusion term of the above equation for class one formation of intermolecular hydrogen bonded complexes. This case is where one of the binary components, the Lewis acid, reacts with the other binary component, the Lewis base, to form a 1:1 complex.

C. Simplifying Assumptions

A mixture of class 1 binaries is really an equilibrium ternary system of Lewis acid, base, and hydrogen bonded complex. This equilibrium ternary system will be assumed to be ideal and has been termed an ideal associated solution. Prigogine[9] and others have used this approach in predicting thermodynamic properties of this type of binary solution.

In order to be certain that there is a true chemical equilibrium between the reacting species, Redlich[21] has indicated that the true criteria for chemical equilibrium is the appearance of a new absorption band that was not present in any of the pure components. For example, in the chloroform-d-ethyl ether system, a band in the infrared appears at 2243 cm^{-1} which is not present in either pure ethyl ether or chloroform.[19]

In an ideal associated solution, derivations from ideality that arise from differences in sizes and shapes of the monomers

and complexes are neglected and heat of solution upon mixing the acid and base is assumed to be the heat of reaction for the formation of the hydrogen bonded complex. With this assumption the $\bar{H}_i$'s of equation (3-5) are related by:

$$\bar{H}_3 - \bar{H}_1 - \bar{H}_2 = \Delta H_r \,, \tag{3-6}$$

where the following subscript nomenclature is used:

1 = Lewis Acid

2 = Lewis Base

3 = Hydrogen Bonded Complex.

Here ΔH is the heat of reaction or the hydrogen bond energy for the reaction:

$$A + B \rightleftarrows AB, \tag{3-7}$$

where A is the Lewis acid and B the Lewis base.

The validity of the above assumption can be tested by comparing the expression derived for the excess Gibb's free energy using the preceeding assumption with experimental data.[10] The agreement between calculated values and the experimental values were close. Sarolea[11] has shown that the assumption of ignoring the difference in sizes of monomers and complex for the system described by equation (3-7) is valid.

The next assumption that will be made is the assumption of local equilibrium. Although heat is flowing through the

fluid as a result of a temperature difference across the fluid, each point in the fluid will be considered to be in chemical equilibrium at its respective temperature and pressure. This assumption has been found to be reasonable.[18] With this assumption, the molar fluxes of each component are related by[12]

$$N_1 = N_2 = -N_3 \tag{3-8}$$

Equation (3-5) then reduces to the following:

$$e = -k_f \frac{\partial T}{\partial z} - \Delta Hc\ D_{3m} \frac{\partial x_3}{\partial z} \tag{3-9}$$

Evaluation of D_{3m} will require cross diffusion coefficient data which is not readily obtainable. However, in the dilute region of $x_1^o = 1$, $D_{3m} = D_{31}^o$ and in the dilute region of $x_1^o = 0$, $D_{3m} = D_{32}^o$ where x_1^o is the apparent mole fraction of the Lewis acid.[13] To avoid dealing with cross diffusion coefficients the following approach will be used.

For sufficiently ideal solutions, the thermal conductivity of the solution might be taken as a mole fraction average of the pure components, which is just linear interpolation. Another form of interpolation is Hermite interpolation where an interpolating polynomial is generated from the value of the function and its slope at several points. Thus if a function f(w) and its slope f'(w) are known at 2 points, w_1 and w_2, then a third order Hermite

interpolating polynomial shown below can be generated. Evaluation

$$f(w) = A + Bw + Cw^2 + Dw^3 \qquad (3\text{-}10)$$

of the constants requires solving four unknowns and four equations. Since the deviation of thermal conductivity from ideality is the principle interest of this work, it will be convenient to define an excess thermal conductivity as:

$$k^E = k_s - x_1^o k_1 - x_2^o k_2 \quad , \qquad (3\text{-}11)$$

where k_s is the solution thermal conductivity, k_1 is the thermal conductivity of the pure Lewis acid, and k_2 is the thermal conductivity of pure Lewis base. Since, $x_1^o + x_2^o = 1$, then equation (3-11) can be written as:

$$k^E = k_s - x_1^o k_1 - (1-x_1^o)k_2. \qquad (3\text{-}12)$$

From the way this function has been defined at $x_1^o = 0$ and $x_1^o = 1$, k^E is zero. If equation (3-12) is differentiated with respect to x_1^o, the following result is obtained:

$$\frac{dk^E}{dx_1^o} = \frac{dk_s}{dx_1^o} + k_2 - k_1 \qquad (3\text{-}13)$$

If it is assumed for the moment that $\frac{dk_s}{dx_1^o}$ can be evaluated at $x_1^o = 0$ and $x_1^o = 1$, then there is enough information available to fit a third order Hermite interpolating polynomial for the excess thermal conductivity function. This equation will take the form:

$$k^E = A + Bx_1^o + Cx_1^{o2} + Dx_1^{o3} . \qquad (3\text{-}14)$$

If this equation is differentiated with respect to x_1^o, then

$$\frac{dk^E}{dx_1^o} = B + 2Cx_1^o + 3Dx_1^{o2} . \qquad (3\text{-}15)$$

At $x_1^o = 0$ equations (3-14) and (3-15) take the form

$$0 = A \qquad (3\text{-}16)$$

and

$$\left.\frac{dk^E}{dx_1^o}\right|_{x_1^o = 0} = B . \qquad (3\text{-}17)$$

At $x_1^o = 1$ equations (3-14) and (3-15) take the form:

$$0 = A + B + C + D \qquad (3\text{-}18)$$

and

$$\left.\frac{dk^E}{dx_1^o}\right|_{x_1^o=1} = B + 2C + 3D. \qquad (3\text{-}19)$$

Solving equations (3-16, 17, 18, and 19) simultaneously results in

$$A = 0 ,$$

$$B = \left.\frac{dk^E}{dx_1^o}\right|_{x_1^o = 0} ,$$

$$C = 2\left.\frac{dk^E}{dx_1^o}\right|_{x_1^o = 0} - \left.\frac{dk^E}{dx_1^o}\right|_{x_1^o = 1} , \text{ and}$$

$$D = \left.\frac{dk^E}{dx_1^o}\right|_{x_1^o = 0} + \left.\frac{dk^E}{dx_1^o}\right|_{x_1^o = 1}$$

If these results are substituted into equation (3-14), the following result is obtained:

$$k^E = \left.\frac{dk^E}{dx_1^o}\right|_{x_1^o=0} x_1^o - x_1^{o2}\left\{2\left.\frac{dk^E}{dx_1^o}\right|_{x_1^o=0} + \left.\frac{dk^E}{dx_1^o}\right|_{x_1^o=1}\right\} + x_1^{o3}\left\{\left.\frac{dk^E}{dx_1^o}\right|_{x_1^o=0} + \left.\frac{dk^E}{dx_1^o}\right|_{x_1^o=1}\right\}$$

At this point if $\frac{dk^E}{dx_1^o}$ can be evaluated at $x_1^o = 0$ and $x_1^o = 1$, then k^E can be calculated over the entire concentration $x_1^o = 0$ to $x_1^o = 1$.

As shown in Appendix A, if the excess thermal conductivity is a cubic or lesser degree function in x_1^o, then approximating k^E with an interpolating polynomial is exact. Several investigators have indicated that thermal conductivity of binary solutions are quadratic functions of compositions.[14,15]

Thus by adopting an interpolation approach the problem of dealing with cross diffusion coefficients is avoided. In the following section, additional reasons will be given for using this approach.

D. Development of an Equation for Predicting Excess Thermal Conductivity

In order to evaluate $\frac{dk^E}{dx_1^o}$ at $x_1^o = 0$ and $x_1^o = 1$, it will be necessary to write equation (3-9) for the regions of $x_1^o = 0$ and $x_1^o = 1$, define a solution thermal conductivity, and then differentiate it with respect to x_1^o.

With the assumption of local equilibrium $\frac{\partial x_3}{\partial z}$ can be written as $\frac{\partial x_3}{\partial T} \frac{\partial T}{\partial z}$ and equation (4-9) becomes:

$$e = - \left[k_f + \Delta Hc \; D_{3m} \frac{\partial x_3}{\partial T} \right] \frac{\partial T}{\partial z} \quad .$$

This equation can be written in terms of a solution thermal conductivity k_s:

$$e = - k_s \frac{\partial T}{\partial z} \quad ,$$

where k_s is defined as:

$$k_s \equiv k_f + \Delta Hc \; D_{3m} \frac{\partial x_3}{\partial T} \quad . \qquad (3\text{-}21)$$

In the region of $x_1^o = 0$ this equation takes the form of

$$k_s \equiv k_f + \Delta Hc\ D_{32}^o\ \frac{\partial x_3}{\partial T} \qquad (3\text{-}22)$$

and in the region of $x_1^o = 1$

$$k_s \equiv k_f + \Delta Hc\ D_{31}^o\ \frac{\partial x_3}{\partial T}\ . \qquad (3\text{-}23)$$

For the reaction $A + B \rightleftarrows AB$ an equilibrium constant will be defined as

$$K = \frac{x_3}{x_1 x_2} \qquad (3\text{-}24)$$

From the stoichiometry of the reaction it can be seen that $n_1 = n_1^o - n_3$ and $n_2 = n_2^o - n_3$ where n_1 and n_2 are respectively the moles of components 1 and 2 present at equilibrium, n_1^o and n_2^o are respectively the apparent number of moles of components 1 and 2, and n_3 is the number of moles of complex present at equilibrium. Substituting for x_1 and x_2:

$$K = \frac{x_3}{[x_3(x_1^o-1)+ x_1^o][x_3(x_2^o-1) + x_2^o]}\ . \qquad (3\text{-}25)$$

The temperature dependence of K can be expressed by the van't Hoff relation:

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}\ . \qquad (3\text{-}26)$$

Equations (3-25) and (3-26) can be combined to give:

$$\frac{dx_3}{dT} = \frac{\frac{K\Delta H}{RT^2}\left[x_1^o\, x_2^o\, (x_3+1)^2 - x_3\right]}{\left[1 - 2Kx_1^o\, x_2^o - 2Kx_1^o\, x_2^o\, x_3 + K\right]} \quad . \qquad (3\text{-}27)$$

In order to evaluate k_f in equations (3-22) and (3-23), k_f, the conduction contribution to the thermal conductivity, will be taken as a mole fraction average of each individual conduction contribution. That is:

$$k_f = x_1k_1 + x_2k_2 + x_3k_3 \ , \qquad (3\text{-}28)$$

where k_1 and k_2 are just the pure component thermal conductivities. The k_3 contribution, that is the contribution from the hydrogen bonded complex, cannot be measured experimentally and must be estimated.

If equations (3-28) and (3-27) are combined with equations (3-22) and (3-23) and then differentiated with respect to x_1^o, the following results are obtained:

at $x_1^o = 0$

$$\left.\frac{dk_s}{dx_1^o}\right|_{x_1^o=0} = \left[\frac{K}{K+1}(k_3-k_1) + k_1-k_2\right]_{x_1^o=0} + \left[\frac{(\Delta H)^2\, D_{32}^o \rho_2}{RT^2\, M_2}\right]_{x_1^o=0} \left[\frac{K}{(K+1)^2}\right]_{x_1^o=0} \qquad (3\text{-}29)$$

and at $x_1^o = 1$

$$\left.\frac{dk_s}{dx_1^o}\right|_{x_1^o=1} = \left[\frac{K}{K+1}(k_2-k_3) + k_1-k_2\right]_{x_1^o=1} - \left[\frac{(\Delta H)^2 D_{31}^o \rho_1}{RT^2 M_1}\frac{K}{(K+1)^2}\right]_{x_1^o=1} \quad (3\text{-}30)$$

When equations (3-29) and (3-30) are incorporated into equation (3-13) the following results are obtained:

$$\left.\frac{dk^E}{dx_1^o}\right|_{x_1^o=0} = \frac{K}{K+1}(k_3-k_1) + \frac{(\Delta H)^2 D_{32}^o \rho_2}{RT^2 M_2}\frac{K}{(K+1)^2} \quad (3\text{-}31)$$

and

$$\left.\frac{dk^E}{dx_1^o}\right|_{x_1^o=1} = \frac{K}{K+1}(k_2-k_3) - \frac{(\Delta H)^2 D_{31}^o \rho_1}{RT^2 M_1}\frac{K}{(K+1)^2} \quad (3\text{-}32)$$

The k_3 contribution will be evaluated by treating the formation of the hydrogen bonded complex as a structural addition to the solute molecule, that is, component 3 is a solute molecule whose mass and volume have been increased. The solute molecule is considered to be the component present in the smaller amount. In the region of $x_1^o = 0$, component 1 is the solute and in the region of $x_1^o = 1$, component 2 will be considered the solute.

Oshida[16] has shown that thermal conductivity is proportional to frequency of the vibration of the molecules and inversely

proportional to the distance between molecular centers. That is:

$$k = \frac{4K\nu}{a} , \tag{3-33}$$

where K is Boltzmann's constant, ν the frequency, and a is the distance between centers which is taken as $(\frac{V}{N})^{\frac{1}{3}}$ where V is the volume per mole and N is Avogadro's number. The ratio $\frac{k_3}{k_1}$ can be written as $\frac{k_3}{k_1} = \frac{\nu_3}{\nu_1}\frac{a_1}{a_3}$ or $\frac{k_3}{k_1} = \frac{\nu_3}{\nu_1}(\frac{V_1}{V_3})^{\frac{1}{3}}$ since $\frac{a_1}{a_3} = (\frac{V_1}{V_3})^{\frac{1}{3}}$.

For the class of hydrogen bonded liquids being studied, the deviation of the solution volume from ideality is less than 1%. Therefore V_3 will be taken as: $V_1 + V_2$ or $V_3 = \frac{M_1}{\rho_1} + \frac{M_2}{\rho_2}$ or

$$(\frac{V_1}{V_3})^{\frac{1}{3}} = \left[\frac{\frac{M_1}{\rho_1}}{\frac{M_1}{\rho_1}+\frac{M_2}{\rho_2}}\right]^{\frac{1}{3}} \quad \text{and} \quad \frac{k_3}{k_1} = \frac{\nu_3}{\nu_1}\left[\frac{\frac{M_1}{\rho_1}}{\frac{M_1}{\rho_1}+\frac{M_2}{\rho_2}}\right]^{\frac{1}{3}} \tag{3-34}$$

Similarly, it can be shown that:

$$\frac{k_3}{k_2} = \frac{\nu_3}{\nu_2}\left[\frac{\frac{M_2}{\rho_2}}{\frac{M_1}{\rho_1}+\frac{M_2}{\rho_2}}\right]^{\frac{1}{3}} . \tag{3-35}$$

The frequency ratios will be evaluated using the Einstein model of a crystal.[17] This assumes there is enough short-range order in the liquid phase for the liquid to be quasi-crystalline.

In the Einstein model, the potential energy of a central molecule has a minimum at the equilibrium or lattice point and varies with the square of the displacement from the equilibrium position. In this model, each molecule vibrates independently of its neighbors and the potential field about the central molecule is spherically symmetrical. This model should be best for dilute solutions, that is, where a large hydrogen bonded complex is surrounded by smaller solvent molecules. Thus the hydrogen-bonded complex in dilute solution vibrates approximately in a spherically symmetric potential field. From the nature of the interpolating polynomial, only dilute solutions need be considered. As shown in Appendix B, the frequency of vibration can be shown to be:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{m}} \quad ,$$

where f is the binding constant, which is similar to a Hooke's law constant, and m is the molecular mass.

The binding constants f for all molecular species will be assumed equal which is consistent with the assumption of ideal associated solution behavior. Using this concept:

$$\frac{\nu_3}{\nu_1} = \sqrt{\frac{M_1}{M_3}} \qquad \text{and} \qquad \frac{\nu_3}{\nu_2} = \sqrt{\frac{M_2}{M_3}} \quad , \quad \text{where}$$

$M_3 = M_1 + M_2$. As shown in Appendix C, the preceding frequency ratio can be shown to be identical to the case where the molecules interact according to the hard sphere model. These results can

be used to put equations (3-34) and (3-35) in the following form:

$$\frac{k_3}{k_1} = R_1 = \sqrt{\frac{M_1}{M_1+M_2}} \sqrt[3]{\frac{\frac{M_1}{\rho_1}}{\frac{M_1}{\rho_1}+\frac{M_2}{\rho_2}}} \qquad (3\text{-}36)$$

$$\frac{k_3}{k_2} = R_2 = \sqrt{\frac{M_2}{M_1+M_2}} \sqrt[3]{\frac{\frac{M_2}{\rho_2}}{\frac{M_1}{\rho_1}+\frac{M_2}{\rho_2}}} \qquad (3\text{-}37)$$

As shown in Appendix D, equation (3-37) can be used to calculate the thermal conductivity of a pair of pure components whose molecules may be considered as rigid and whose binding constants are equal. This requires that the components have similar shapes and sizes.

In the region of $x_1^o = 0$, k_3 will be evaulated using equation (3-36) and by using equation (3-37) in the region of $x_1^o = 1$. Using these results in equations (3-31) and (3-32) results in:

$$\left.\frac{dk^E}{dk_1^o}\right|_{x_1^o=0} = \frac{K}{K+1} k_1 [R_1-1] + \frac{(\Delta H)^2 D_{32}^o \rho_2}{RT^2 M_2} \frac{K}{(K+1)^2} \qquad (3\text{-}38)$$

$$\left.\frac{dk^E}{dx_1^o}\right|_{x_1^o=1} = \frac{K}{K+1} k_2 [1-R_2] - \frac{(\Delta H)^2 D_{31} \rho_1}{RT^2 M_1} \frac{K}{(K+1)^2} \qquad (3\text{-}39)$$

At this point with expressions for $\frac{dk^E}{dx_1^o}$ at $x_1^o = 0$ and $x_1^o = 1$, equation (3-20) can be checked with experimental data. Substituting $\frac{dk^E}{dx_1^o}$ into equation (3-20) results in:

$$k^E = \{\frac{(\Delta H)^2 D_{32}^o \rho_2}{RT^2 M_2} \frac{K}{(K+1)^2} + \frac{K}{K+1} k_1 [R_1-1]\}\{x_1^o - 2x_1^{o2}+x_1^{o3}\}$$

$$+ \{-\frac{(\Delta H)^2 D_{31}^o \rho_1}{RT^2 M_1} \frac{K}{(K+1)^2} + \frac{K}{K+1} k_2 [1-R_2]\}\{-x_1^{o2} + x_1^{o3}\} \quad (3\text{-}40)$$

Equation (3-40) allows the prediction of the excess thermal conductivity from a knowledge of the equilibrium constant, pure component thermal conductivities, molecular weights, densities, diffusion coefficients, and the hydrogen bond energies. However, it must be remembered that equation (3-40) was derived only for binary solutions whose components form 1:1 hydrogen bonded complexes.

E. Recapitulation of Simplifying Assumptions

In developing equation (3-40) the following assumptions have been made:

1. The 1:1 complex formed by the reaction of Lewis acid and base is a distinct molecular specie. This assumption has been used in developing means of predicting thermodynamic properties of these types of solutions and the results

agree reasonably well with experiment. Also, x-ray, electron, and neutron diffraction studies have indicated that the hydrogen bond formed between two molecules results in a specific distance and orientation between the two molecules.

2. Each point in the fluid is assumed to be in local equilibrium. That is, at equilibrium at its particular conditions. This assumption is reasonable since hydrogen bonded equilibrium is very fast and reversible.

3. The isothermal diffusion coefficients will be taken to be the same as the diffusion coefficients in a non-isothermal system. This assumption has been made in the treatment of the thermal conductivity of reacting gases.

4. The frequency ratio between hydrogen bonded complex and the pure components is evaluated from the Einstein model of a crystal. In this model, each molecule vibrates independently of its neighbors and the potential field about a central molecule is spherically symmetrical. In the dilute regions where the frequency ratios are being considered, this assumption is best since the larger complex molecule is surrounded by solvent molecules all of the same type.

5. The molecular volume of the complex is taken as the sum of the molecular volumes of the reactants. This

assumption appears to be reasonable since the volume change on mixing the reactants is less than 1%.

6. The equilibrium mixture of Lewis acid, Lewis base, and hydrogen bonded complex is considered to be ideal.

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CHAPTER 4
DESCRIPTION OF APPARATUS AND OPERATING PROCEDURE

A. Description of Apparatus

The apparatus used to measure the thermal conductivity of the binary solutions was one designed by Sakiadis and Coates.[1] This apparatus is a steady state parallel plate apparatus in which the distance between the plates or the test liquid thickness can be varied. A drawing of the apparatus is shown in Figure 2. The cell and supporting equipment are shown in Figures 3 through 8. The distance between the plates and the temperature drop across the liquid film are kept small in order to eliminate convective and radiation effects. Also, the heat flow is in the downward direction in order to minimize convection. The apparatus is thermally guarded in order to eliminate radial heat losses.

The liquid sample is enclosed between 2 cylindrical steel bars held in an upright pyrex tube. The bottom bar is cooled and the top bar is heated. The cooling and heating of the bars is achieved by circulating thermostated water through them. The liquid film thickness is adjusted by raising or lowering the hot bar. Temperatures in the hot bar, cold bar, and the outside surface of the pyrex tube are determined by means of calibrated thermocouples, a potentiometer, and null balance. The apparatus is thermally guarded to eliminate radial heat losses.

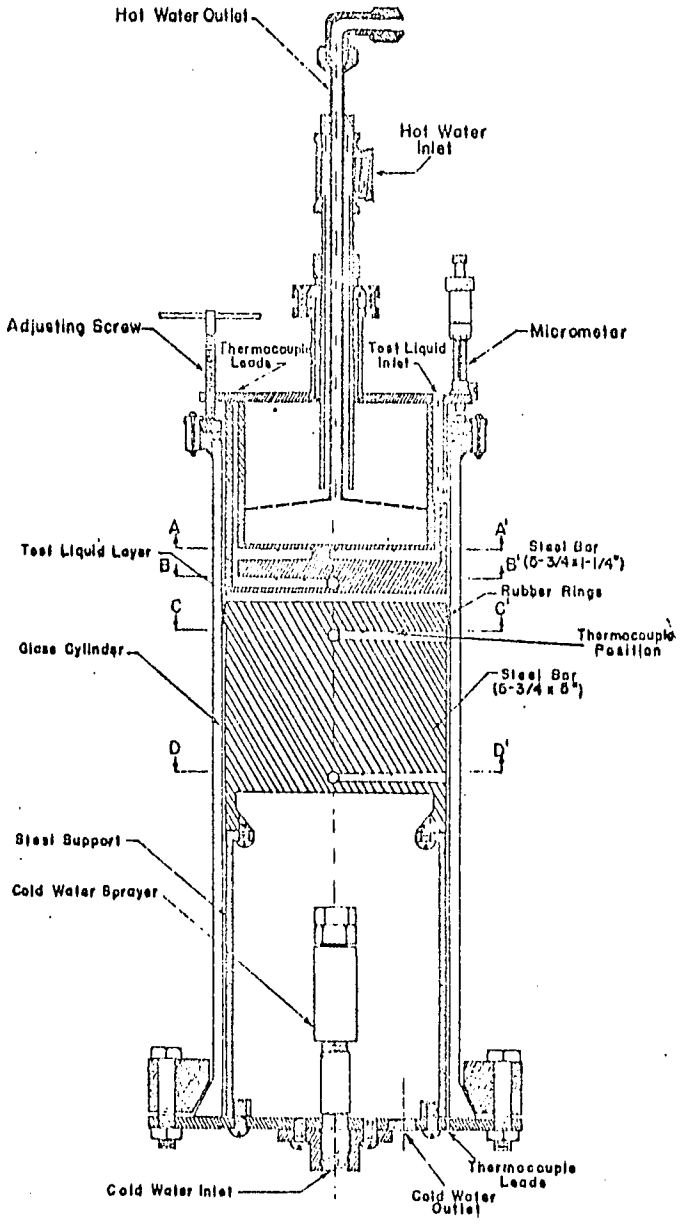
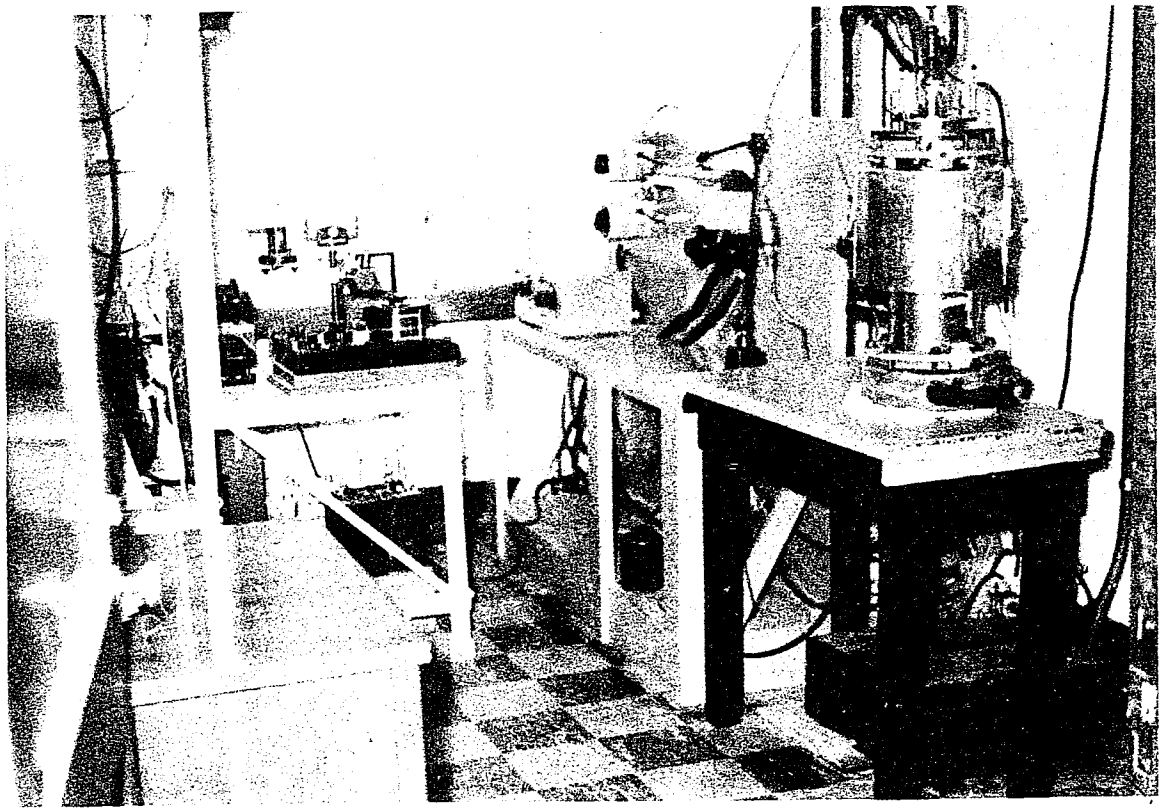


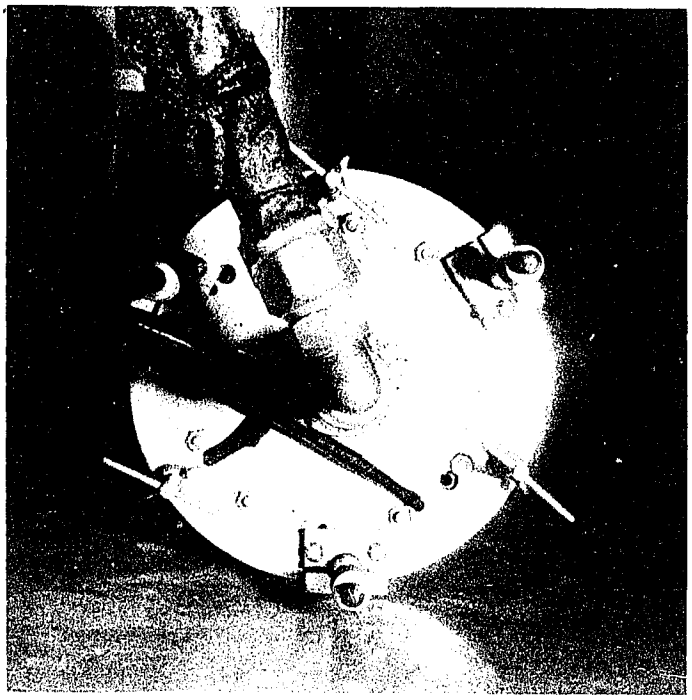
FIGURE 2

THERMOCONDUCTIMETRIC APPARATUS FOR LIQUIDS



General View

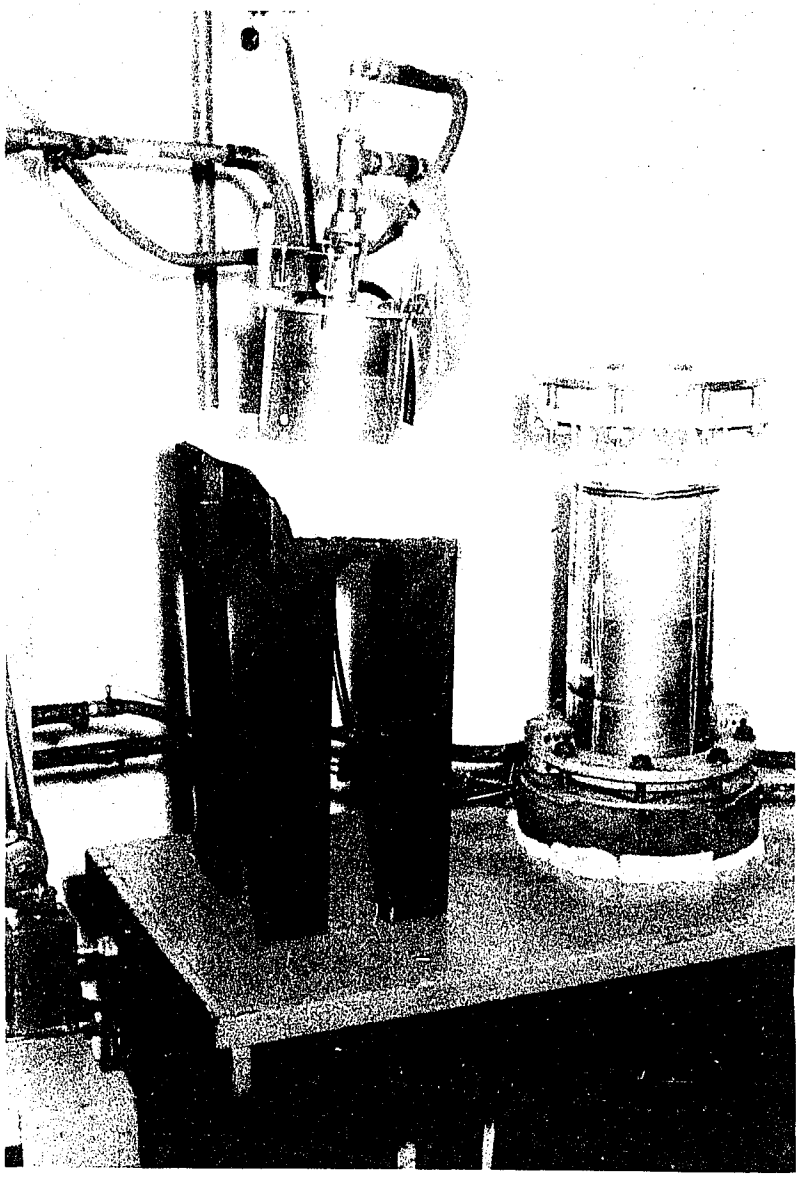
Figure 3



Top View of Hot Bar, Water Connections,

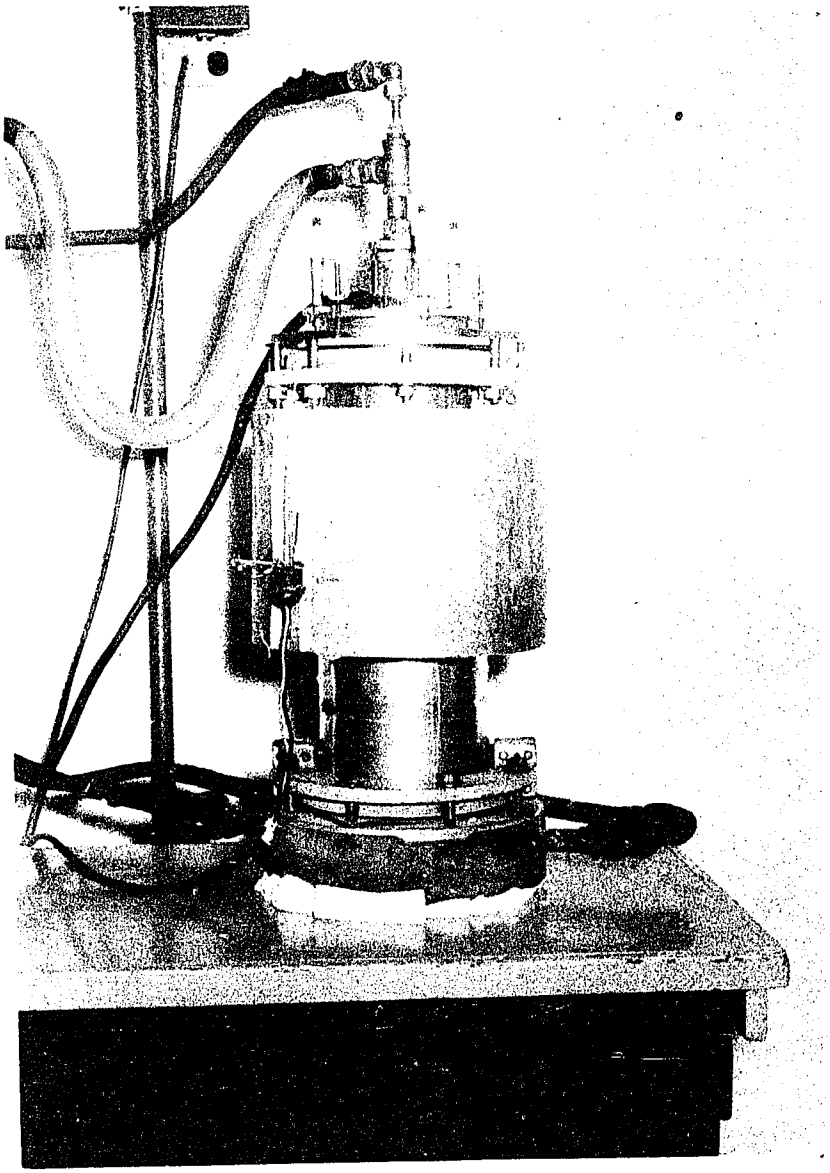
Micrometers, and Jack Screws

Figure 4



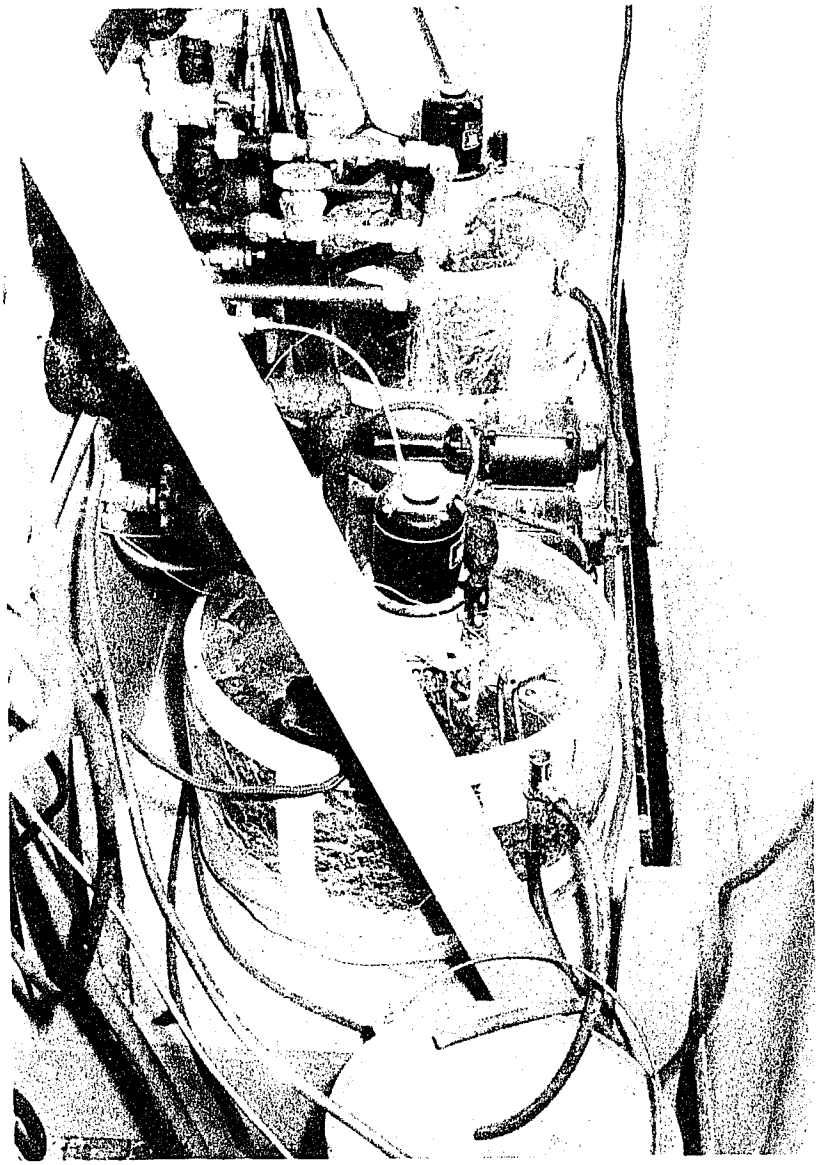
Cell Disassembled

Figure 5



Cell Assembled

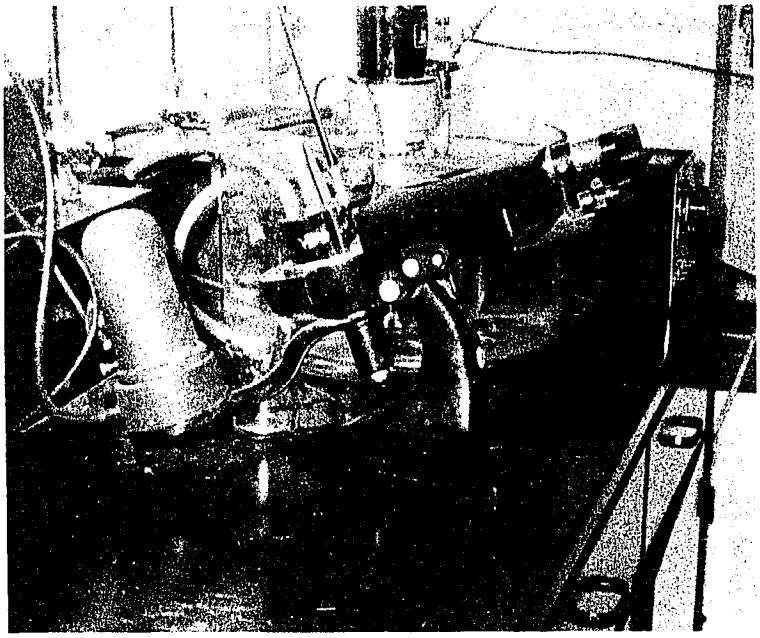
Figure 6



Hot and Cold Water Baths, Water Circulators,

and Thermoregulators

Figure 7



Precision Refractometer

Figure 8

The hot bar is made from a steel shaft 5.731 inches in diameter and 1.25 inches long. This bar is connected to a piece of steel pipe of the same diameter which in turn is bolted to a steel plate. The hot bar, pipe, and plate form a chamber in which water from the hot bath is circulated. The chamber is equipped with a baffle and concentric inlet and outlet pipes to insure that the hot bar is heated evenly. Five copper-constantan thermocouples are soldered in two taper pins which are imbedded in the hot bar. The distance from the outer surface of the hot bar to the thermocouple plane is 0.400 inches.

The cold bar was made from the same steel shaft as the hot bar. The diameter of the cold bar is 5.731 in. and the length is 5.000 in. The cold bar is attached to a piece of pipe the same diameter as the cold bar which in turn is attached to a steel plate. The cold bar, pipe, and plate form a chamber in which water from the cold bath is circulated. The chamber is equipped with a spray to distribute the cold water evenly over the bottom of the cold bar. The cold bar has 10 copper-constantan thermocouples in 2 planes. The distance between the 2 planes is 3.7432 in. The distance between the outer surface of the cold bar and the middle thermal couple layer is 0.73 in. as shown in Figure 2.

The liquid level thickness is set by means of 3 jack screws that thread through the steel plate that forms the water chamber of the hot bar. These jack screws bear on the steel flange attached to the lip of the pyrex tube. These screws

are arranged 120° apart. Three micrometers are equally spaced between each screw. The liquid thicknesses are determined by taking differences of the readings of the micrometers with the bars together and with the hot bar raised.

Three thermocouples for determining radial heat losses are located on the outside surface of the pyrex pipe. Two of them are opposite the thermocouples in the cold bar and the third is located midway between them. Radial heat loss correction can be made by use of cooling coils wrapped around the surface of the pyrex pipe or resistance heaters in an insulating jacket surrounding the pyrex pipe.

The annular space between the cold bar and pyrex pipe is sealed with 2 "O" rings. The bottom "O" ring is rubber and the upper one is teflon. The annular space between the hot bar and the pyrex tube and above the liquid level is sealed with a single rubber "O" ring.

The hot and cold bath temperatures are controlled by 2 E.H. Sargent Inc. electrical relays operating with mercury thermoswitches made by the American Instrument Co. These thermoswitches are capable of controlling bath temperatures to within ±.005 C.

Two Eastern Industries centrifugal pumps are used to circulate water from the baths to the hot and cold bars. Tubing from the pump discharges is flexible tygon tubing in order to eliminate vibrations caused by the pumps.

The equipment used in making the e.m.f. readings is: a K-2 Leeds and Northrup Potentiometer readable to .1 microvolt, a Honeywell Electronik Null Indicator with a rated sensitivity of 1 microvolt/mm., a Leeds and Northrup constant voltage source for the potentiometer, and an Eppley standard cell.

Solution compositions are determined with a Bausch and Lomb precision refractometer kept at 25°C with a Sargent constant temperature bath.

B. Procedure

1. Set mercury thermoswitches to the desired temperatures.
2. Turn on refrigerator, coolant pump, thermoregulator relays, and auxiliary heaters.
3. Adjust thermoregulator relays such that each relay has approximately equal off and on time.
4. Turn on potentiometer voltage supply and null balance meter. These instruments require about 30 minutes of warm-up time.
5. Turn on circulating pumps and allow bars to come into equilibrium with water baths.
6. Pour about 100 ml. of sample into cell.
7. Lower hot bar so it rests on cold bar without air being trapped in the sample.
8. Take micrometer readings with hot bar down and then raise hot bar to give an approximate value of the desired liquid thickness.

9. Slide the rubber sealing ring down.
10. Make approximate correction for radial heat losses.
11. Let apparatus run for 30 minutes.
12. Lower hot bar rapidly until it rests on cold bar and take micrometer readings.
13. Raise hot bar until desired liquid thickness is obtained. Lower the sealing ring.
14. Let apparatus run for about one hour to come to equilibrium. During this time correct for radial heat losses. Radial heat losses are negligible when the algebraic sum of jacket thermocouple readings and their corresponding bar thermocouple readings are less than 20 microvolts.
15. Take thermocouple readings. When consecutive readings of each layer agree within 0.5 microvolts over a one-half hour period, equilibrium has been reached.
16. Read micrometers with bar up.
17. Lower bar rapidly and take micrometer readings.
18. Repeat steps 14 and 15 with hot bar resting on the cold bar.

CHAPTER 4 REFERENCES

[1]B. C. Sakiadis and J. Coates, Studies of Thermal Conductivity of Liquids (Baton Rouge, Louisiana, Engineering Experiment Station, Louisiana State University, 1954), Bulletin No. 45, p. 28.

CHAPTER 5
EXPERIMENTAL RESULTS

Experimental data was collected for the binary systems: methyl ethyl ketone-chloroform, isopropyl ether-chloroform, methyl-ethyl ketone-1,2 dichloroethane, diethyl ketone-chloroform, methyl isobutyl ketone-chloroform, and toluene-chloroform. The thermal conductivity values have been corrected to 25°C and are shown in Figures 9 through 14. Smoothed experimental data uncorrected for temperature are shown in appendix The temperature coefficients were obtained by taking mole fraction averages of the pure component temperature coefficients, which were obtained from the literature.[1,2]

Experimental data was taken from the literature for the following systems: chloroform-acetone, chloroform-ethyl ether, and chloroform-benzene. The chloroform-acetone data is that of Rodriguez.[3] The chloroform-ethyl ether data was obtained by Fillippov[4] and converted to 25°C by Rodriguez.[3] The chloroform-benzene data is that of Riedel[5] and has been tabulated by Jordan.[6]

The excess thermal conductivity data was obtained from the smoothed experimental thermal conductivity data of Tables I through IX by using the definition of excess thermal conductivity. The excess thermal conductivity data for the systems taken from

the literature, i.e. acetone-chloroform, ethyl ether-chloroform, and benzene-chloroform, were obtained in the same fashion.

Table I

Solution Thermal Conductivity

for Methyl Ethyl Ketone-Chloroform

Mole Fraction Chloroform	Solution Thermal Conductivity	Excess Thermal Conductivity
0.0	0.0870	0.00000
0.1	0.0823	-0.00271
0.2	0.0782	-0.00482
0.3	0.0748	-0.00623
0.4	0.0720	-0.00704
0.5	0.0696	-0.00745
0.6	0.0676	-0.00746
0.7	0.0661	-0.00697
0.8	0.0654	-0.00568
0.9	0.0658	-0.00329
1.0	0.0671	0.00000

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).
The data have been corrected to 25^{o}C.
The excess thermal conductivity has been calculated from equation (3-11).

Table II

Solution Thermal Conductivity

for Acetone-Chloroform

Mole Fraction Chloroform	Solution Thermal Conductivity	Excess Thermal Conductivity
0.0	0.0930	0.00000
0.1	0.0876	-0.00297
0.2	0.0825	-0.00564
0.3	0.0784	-0.00731
0.4	0.0750	-0.00828
0.5	0.0723	-0.00855
0.6	0.0700	-0.00842
0.7	0.0686	-0.00739
0.8	0.0677	-0.00586
0.9	0.0675	-0.00363
1.0	0.0687	0.00000

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).
The temperature is 25^{o}C.
The excess thermal conductivity has been calculated from equation (3-11).

Table III

Solution Thermal Conductivity

for Benzene-Chloroform

Mole Fraction Chloroform	Solution Thermal Conductivity	Excess Thermal Conductivity
0.0	0.0850	0.00000
0.1	0.0815	-0.00177
0.2	0.0781	-0.00344
0.3	0.0753	-0.00451
0.4	0.0728	-0.00528
0.5	0.0710	-0.00535
0.6	0.0696	-0.00502
0.7	0.0684	-0.00449
0.8	0.0674	-0.00376
0.9	0.0671	-0.00233
1.0	0.0677	0.00000

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).
The temperature is 68^{o}F.
The excess thermal conductivity has been calculated from equation (3-11).

Table IV

Solution Thermal Conductivity

for 1,2 dichloroethane-Methyl Ethyl Ketone

Mole Fraction 1,2 dichloroethane	Solution Thermal Conductivity	Excess Thermal Conductivity
0.0	0.0870	0.00000
0.1	0.0849	-0.00121
0.2	0.0830	-0.00222
0.3	0.0816	-0.00273
0.4	0.0803	-0.00314
0.5	0.0793	-0.00325
0.6	0.0785	-0.00316
0.7	0.0780	-0.00277
0.8	0.0777	-0.00218
0.9	0.0777	-0.00129
1.0	0.0781	0.00000

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).
The data have been corrected to 25^{o}C.
The excess thermal conductivity has been calculated from equation (3-11).

Table V

Solution Thermal Conductivity

for Ethyl Ether-Chloroform

Mole Fraction Chloroform	Solution Thermal Conductivity	Excess Thermal Conductivity
0.0	0.0799	-0.00000
0.1	0.0769	-0.00206
0.2	0.0741	-0.00392
0.3	0.0717	-0.00538
0.4	0.0696	-0.00654
0.5	0.0676	-0.00760
0.6	0.0665	-0.00776
0.7	0.0671	-0.00622
0.8	0.0679	-0.00448
0.9	0.0690	-0.00244
1.0	0.0705	0.00000

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).
The excess thermal conductivity has been calculated from equation (3-11).
The temperature is 25^{o}C.

Table VI

Solution Thermal Conductivity

for Isopropyl Ether-Chloroform

Mole Fraction Chloroform	Solution Thermal Conductivity	Excess Thermal Conductivity
0.0	0.0608	0.00000
0.1	0.0600	-0.00143
0.2	0.0594	-0.00266
0.3	0.0593	-0.00339
0.4	0.0595	-0.00382
0.5	0.0600	-0.00395
0.6	0.0608	-0.00378
0.7	0.0618	-0.00341
0.8	0.0630	-0.00284
0.9	0.0646	-0.00187
1.0	0.0671	0.00000

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).
The data have been corrected to 25^{o}C.
The excess thermal conductivity has been calculated from equation (3-11).

Table VII

Solution Thermal Conductivity

for Diethy Ketone-Chloroform

Mole Fraction Chloroform	Solution Thermal Conductivity	Excess Thermal Conductivity
0.0	0.0832	0.00000
0.1	0.0795	-0.00209
0.2	0.0767	-0.00328
0.3	0.0743	-0.00407
0.4	0.0723	-0.00446
0.5	0.0706	-0.00455
0.6	0.0693	-0.00424
0.7	0.0683	-0.00363
0.8	0.0676	-0.00272
0.9	0.0672	-0.00151
1.0	0.0671	0.00000

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).
The data have been corrected to 25^{o}C.
The excess thermal conductivity has been calculated from equation (3-11).

Table VIII

Solution Thermal Conductivity

for Toluene-Chloroform

Mole Fraction Chloroform	Solution Thermal Conductivity	Excess Thermal Conductivity
0.0	0.0787	0.00000
0.1	0.0758	-0.00174
0.2	0.0732	-0.00318
0.3	0.0710	-0.00422
0.4	0.0688	-0.00526
0.5	0.0669	-0.00600
0.6	0.0655	-0.00624
0.7	0.0647	-0.00588
0.8	0.0645	-0.00492
0.9	0.0652	-0.00306
1.0	0.0671	0.00000

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).
The data have been corrected to 25^{o}C.
The excess thermal conductivity has been calculated from equation (3-11).

Table IX

Solution Thermal Conductivity

for Methyl Isobutyl Ketone-Chloroform

Mole Fraction Chloroform	Solution Thermal Conductivity	Excess Thermal Conductivity
0.0	0.0739	0.00000
0.1	0.0723	-0.00092
0.2	0.0709	-0.00164
0.3	0.0696	-0.00226
0.4	0.0685	-0.00268
0.5	0.0675	-0.00300
0.6	0.0666	-0.00322
0.7	0.0659	-0.00324
0.8	0.0653	-0.00316
0.9	0.0655	-0.00228
1.0	0.0671	0.00000

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).
The data have been corrected to 25^{o}C.
The excess thermal conductivity has been calculated from equation (3-11).

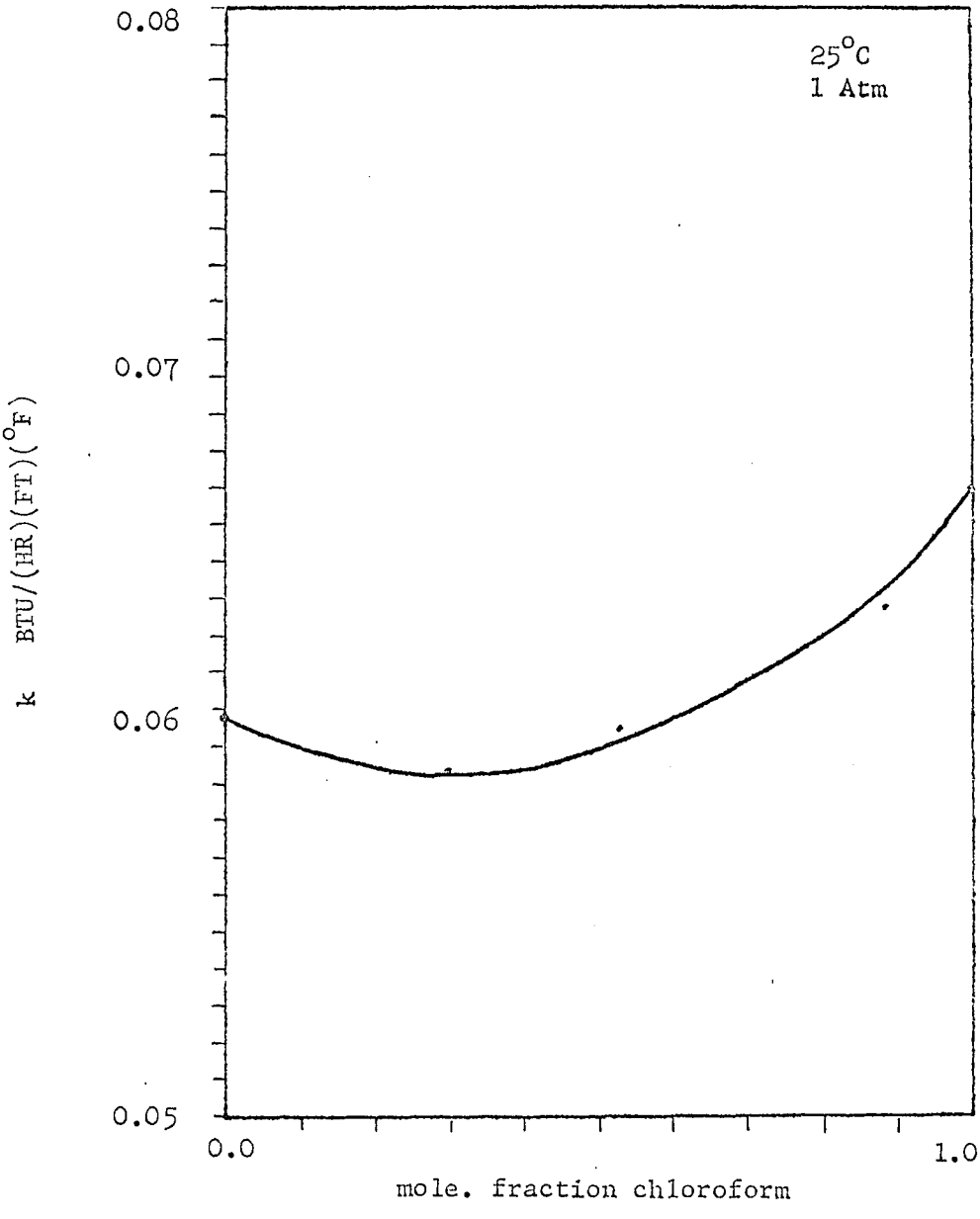


Fig.9 Thermal Conductivity versus composition for mixtures of isopropyl ether and chloroform at 25°C and 1 atm.

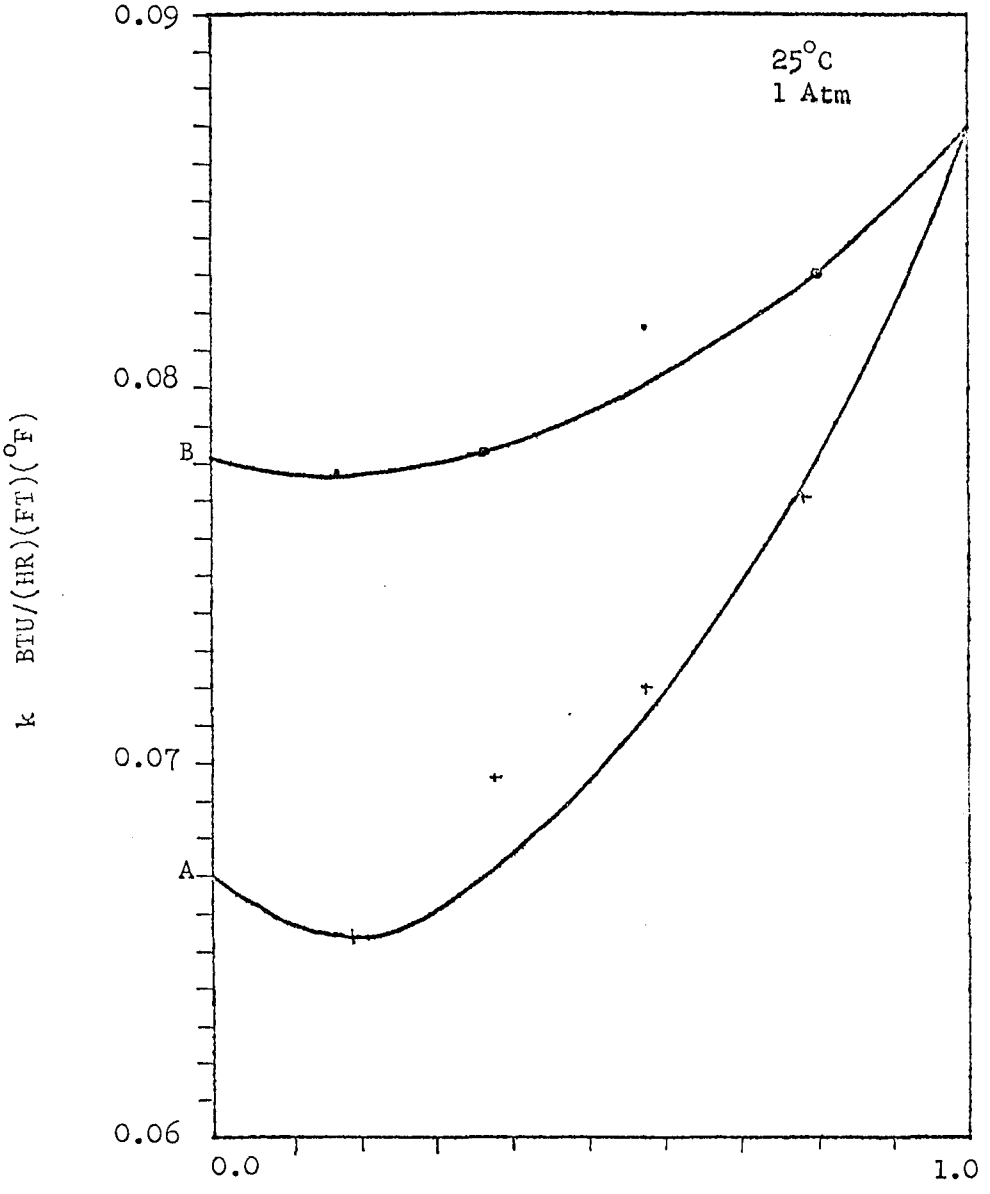


Fig. 10 Thermal Conductivity versus composition. Curve A - mixtures of methyl ethyl ketone and chloroform. Curve B - mixtures of methyl ethyl ketone and 1,2 dichloroethane.

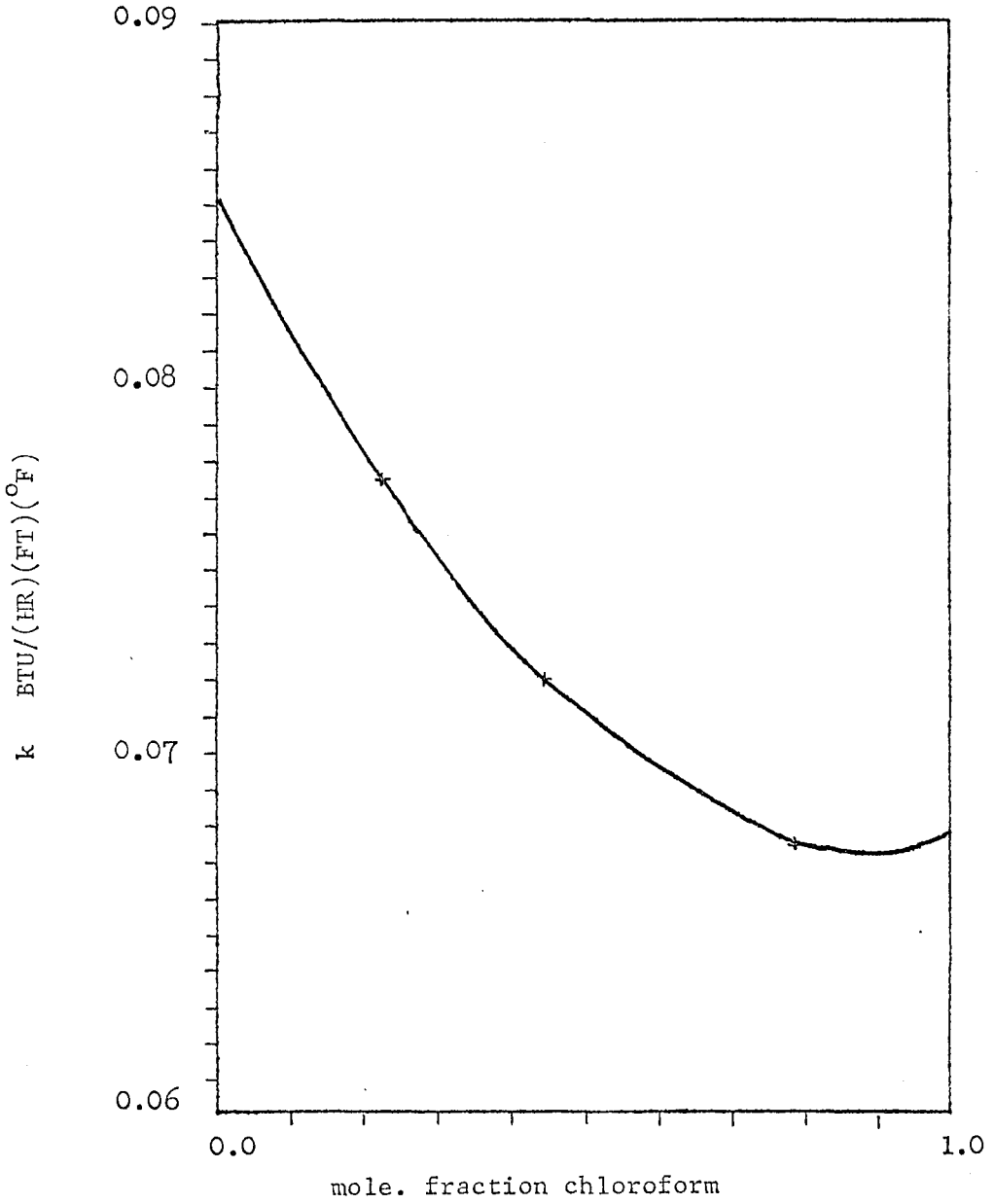


Fig. 11 Thermal Conductivity versus composition for mixtures of benzene and chloroform at 20°C and 1 atm. Data taken from references 5 and 6.

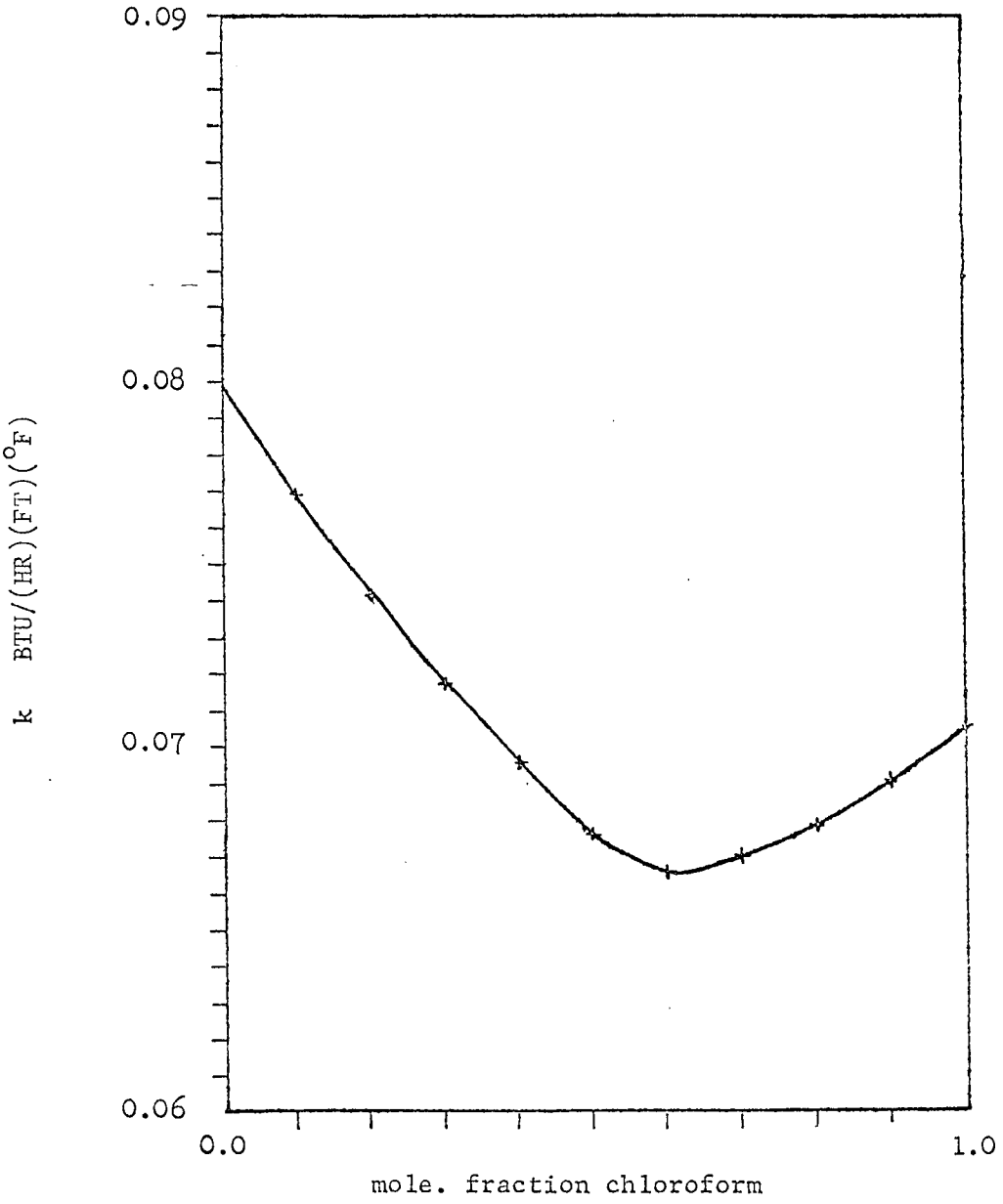


Fig. 12 Thermal Conductivity versus composition for mixtures of ethyl ether and chloroform at 25°C and 1 atm. Data taken from references 3 and 4.

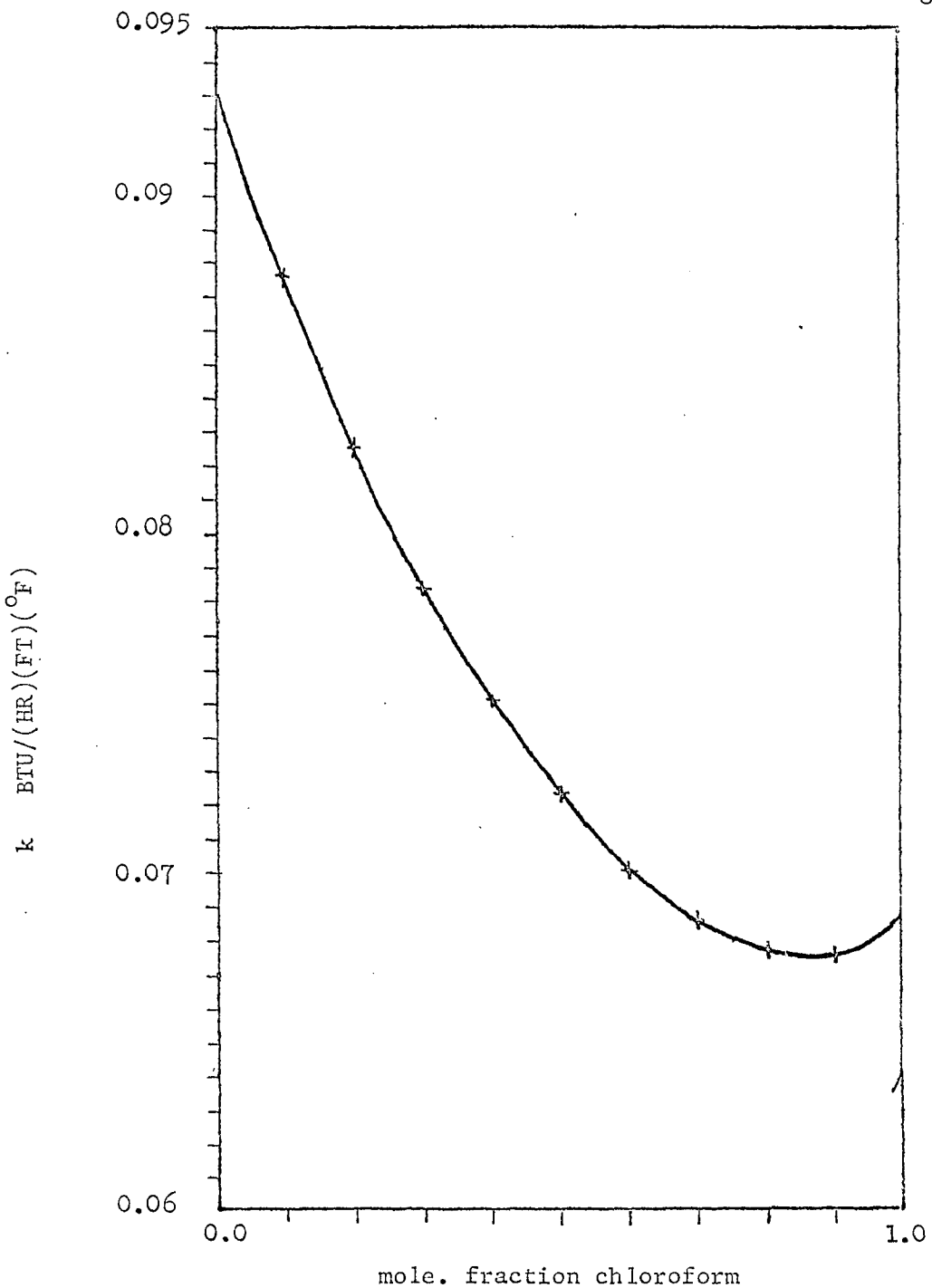


Fig. 13 Thermal Conductivity versus composition for mixtures of acetone and chloroform at 25°C and 1 atm. Data taken from reference 3.

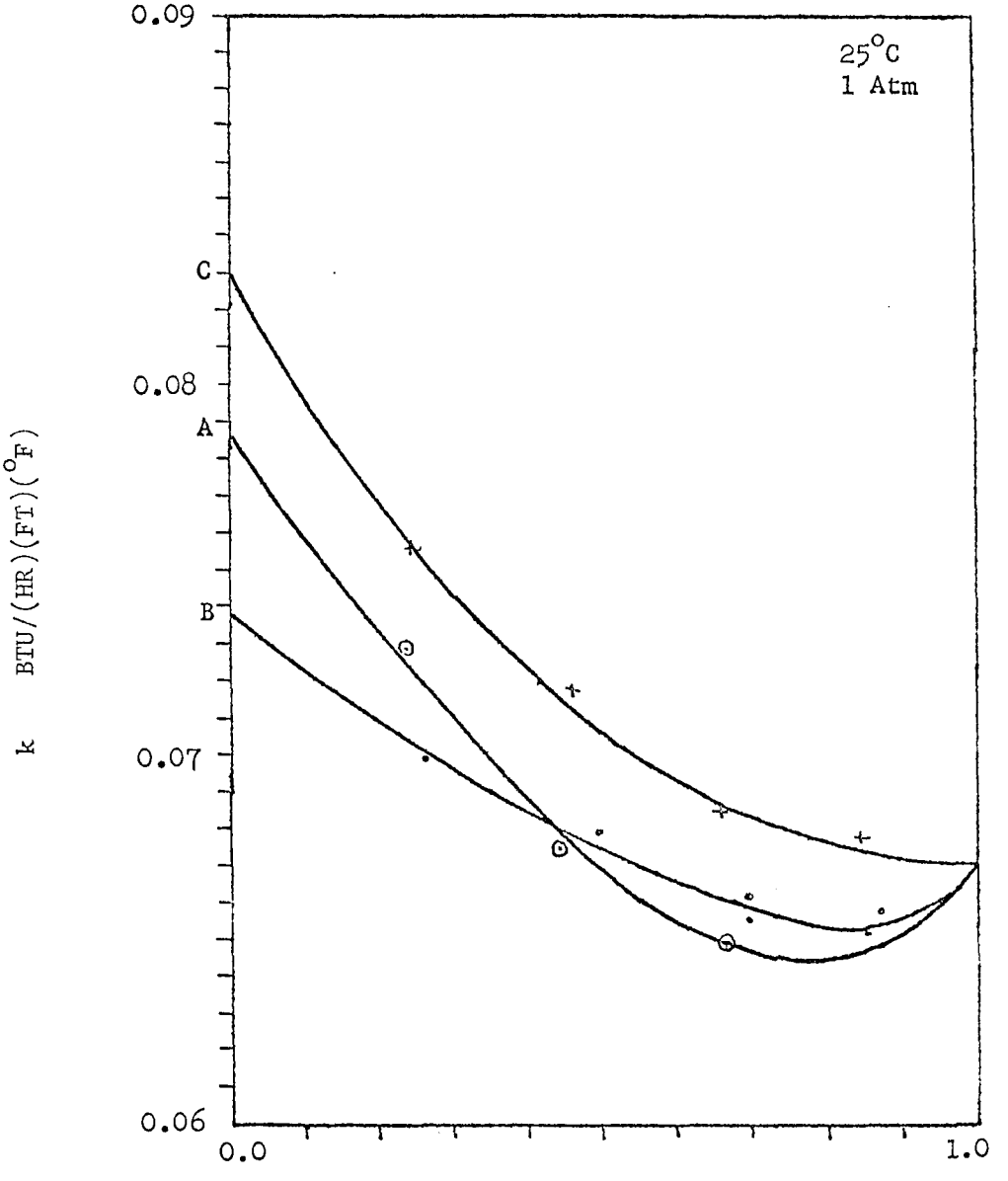


Fig. 14 Thermal Conductivity versus composition. Curve A - mixtures of chloroform and toluene. Curve B - mixtures of chloroform and methyl isobutyl ketone. Curve C - mixtures of chloroform and diethyl ketone.

CHAPTER 5 REFERENCES

[1]B. C. Sakiadis and J. Coates, A Literature Survey of the Thermal Conductivity of Liquids (Baton Rouge, Louisiana: Engineering Experiment Station, Louisiana State University, 1952), Bulletin No. 34, p. 26.

[2]B. C. Sakiadis and J. Coates, "Studies of the Thermal Conductivity of Liquids," A.I.Ch. E. J., I(1955), p. 280.

[3]H. V. Rodriguez, Molecular Field Relationships to Liquid Viscosity, Compressibility, and Prediction of Thermal Conductivity of Binary Liquid Mixtures (Ph.D. Dissertation, Louisiana State University, 1962).

[4]L. P. Fillippov and N. S. Novoselova, "The Thermal Conductivity of Solutions of Normal Mixtures," Vestnik Moskovskogo Universiteta, Seriya Fiziko-Matenatecheskikhi Estestvennykk Nauk, No. 3, X(1955), p. 37.

[5]L. Riedel, Mitteilungen tes Kaltetechnischen Instituts und der Reichforchungs-Anstalt fur Lebensmittelfrischaltung an der Technischen Hochschule Karlsruhe, No. 2, 1947, p. 45.

[6]H. B. Jordan, Prediction of Thermal Conductivity of Miscible Binary Liquid Mixtures from the Pure Component Values (Masters Thesis, Louisiana State University, 1961), p. 22.

CHAPTER 6
DISCUSSION OF RESULTS

A. Discussion of Errors

The absolute error in the experimental determination of thermal conductivity has been determined by Sakiadis[1] to be ±1.5% where about 1% of this is due to a consistent error in determining the thermal conductivity of steel in the hot and cold bars of the apparatus. The precision of the apparatus has been found to be ±0.23% at the 99.5% confidence level. Since the apparatus was run at essentially the same conditions, the error in determining the excess thermal conductivity should be about ±0.5%. As can be seen from Fig. 16 to 23, the error in the excess thermal conductivity is well within the experimental values of excess thermal conductivity.

Comparison of equation (3-40) with the experimental excess thermal conductivity data is shown in Fig. 16 to 23 and Tables XI to XIX. The percent error shown in the tables has been defined as:

$$\% \text{ error} = \frac{\left| k_{\text{experimental}} - k_{\text{theoretical}} \right|}{k_{\text{experimental}}}$$

B. Qualitative Discussion of Results

Several investigators[3,4] have found that steric hindrance decreases the extent of hydrogen bonding, which should result in

a smaller equilibrium constant. According to equation (3-40), a smaller equilibrium constant results in smaller values of excess thermal conductivity. The experimental data supports this conclusion. For example in a binary solution of chloroform and a ketone, as the steric hindrance around the oxygen on the ketone increases, the excess thermal conductivity decreases. This is shown in Table X. The same is true where the base is an ether. Isopropyl ether-chloroform solution which has an oxygen more hindered than with ethyl ether, has a smaller excess thermal conductivity.

The data of Barnette[5] also indicates that as steric hindrance increases in hydrogen bonded systems the excess thermal conductivity decreases. Smith and Creitz[4] have shown from the infrared spectra for several alcohols that the hydrogen bond equilibria tends toward the monomer form rather than the chain form as the size and complexity of the alcohol molecule increases. The data of Barnette show that the excess thermal conductivity decreases as the size of the alcohol increases, that is, for the binary solutions formed from methanol, ethanol, n-propanol, and isopropanol dissolved in inert solvents, methanol solutions had the highest excess thermal conductivity, followed by ethanol, n-propanol, and iso-propanol. These findings tend to support the conclusion that the formation of hydrogen bonds is the major contribution to the excess thermal conductivity.

C. Spectroscopic Evidence for the Formation of Bimolecular Hydrogen Bonded Complexes

Spectroscopic evidence indicates that the binary systems outlined in chapter five are of the type that permit equation (3-40)

to be tested with experimental data, that is, these are systems that form a bimolecular complex from the reaction of an acid and base. Lord, Nolan, and Stidham[6] obtained infrared spectra for chloroform-ketone and chloroform-ether solutions and have concluded that a hydrogen bond is formed between the proton of chloroform and the oxygen of the ether or ketone. The same conclusion has been reached by Rezaev and Shchepanyak,[7] who have obtained the Raman spectra for chloroform-ether and chloroform-ketone systems. Reeves and Schneider[8] have obtained the nuclear magnetic resonance spectra for chloroform and aromatics and have confirmed the existence of hydrogen bonded complexes. The complexes formed are bimolecular complexes consisting of chloroform and aromatics with the hydrogen of the chloroform oriented toward the plane of the aromatic ring and the chlorine atoms directed away from the ring. Tamres[9] has studied aromatic-chloroform solutions by infrared methods and has reached the same conclusion. Chelkowski[14] has studied binary solutions of 1,2 dichloroethane by dielectric saturation methods and has concluded that 1,2 dichloroethane can form a hydrogen bond with donor molecules.

D. Sources of Data for Calculating Excess Thermal Conductivity

The diffusivity data necessary for use in Equation (3-40) was obtained by the method of Wilke and Chang.[11] In using this method, the molal volume of the hydrogen bonded complex was taken as the sum of the molal volume of the Lewis acid and base.

The hydrogen bond energy for the O-H bond was taken as -4070 cal/gm. mole from the work of Sherman.[12] This agrees closely

with the value of -4300 cal/gm. mole reported by Rezaev and Schepanyak[9] for several systems. The hydrogen bond energy for H-aromatic was taken as -2040 cal/gm. mole from the work of Barker.[13] This value agrees closely with the value of -1970 cal/gm. mole reported by Creswell and Allred.[10]

The hydrogen bond equilibrium constants can be obtained by spectroscopic measurements or from activity coefficient data. The method for obtaining the equilibrium constant from activity coefficients is outlined in Appendix E . The equilibrium constants obtained from spectroscopic measurements should be better than those from activity coefficient data since concentrations are measured specifically in the former method.

For the chloroform-acetone system, the equilibrium constant used in predicting excess thermal conductivity was 7.6. This value was reported by Bystrov from the nuclear magnetic resonance spectra. No data could be found with which to evaluate an equilibrium constant for the methyl ethyl ketone- chloroform. Since methyl ethyl ketone is similar to acetone, the same equilibrium was used for the methyl ethyl ketone- chloroform as the acetone-chloroform system. Rezaev and Shchepanyak[7] have obtained the Raman spectra for the ethyl ether-chloroform system and report a value of 5.25. For the chloroform-toluene system, an equilibrium constant of 3.68 was obtained from vapor-liquid equilibrium data.[15] An equilibrium constant was evaluated for the system acetone-1,2 dichloroethane system from vapor liquid equilibrium data[16] and was found to be 0.43. Since methyl ethyl ketone is similar to acetone, this value was used for the methyl ethyl

ketone-1,2 dichloroethane system since no data on this system was available. The chloroform-isopropyl ether nuclear magnetic resonance spectra has been studied and a equilibrium constant of 2.06 has been reported,[17] and likewise for the benzene-chloroform an equilibrium constant of 1.06 has been reported.[10]

Equilibrium constants were not obtainable for the systems diethyl ketone-chloroform and methyl isobutyl ketone-chloroform. Values of equilibrium constants were obtained by fitting an equilibrium constant to the excess thermal conductivity data. The values obtained in this fashion were 1.50 for the diethyl ketone-chloroform and 0.75 for methyl isobutyl ketone-chloroform system. These values are considerably lower than the equilibrium constant for the chloroform-acetone system which is 7.6. This is to be expected since oxygen on the methyl isobutyl ketone and diethyl ketone molecules is considerably more sterically hindered than the oxygen molecule on the acetone molecule.

Table X

Effect of Increasing Steric Hindrance on the Excess Thermal Conductivity for Several Ketone-Chloroform Solutions

Base	k^{E}_{max} (BTU)/(HR)(FT)(^{o}F)
Acetone	-0.0086
Methyl Ethyl Ketone	-0.0075
Diethyl Ketone	-0.0046
Methyl Isobutyl Ketone	-0.0032

Table XI

Predicted Versus Experimental Excess Thermal Conductivity

for the Chloroform-Isopropyl Ether System

Mole Fraction Chloroform	Predicted Excess Thermal Conductivity	Experimental Excess Thermal Conductivity	Percent Error
0.0	0.0000	0.0000	0.00
0.1	-0.0018	-0.0014	28.6
0.2	-0.0032	-0.0027	18.5
0.3	-0.0041	-0.0034	20.6
0.4	-0.0045	-0.0038	18.4
0.5	-0.0046	-0.0040	15.0
0.6	-0.0043	-0.0038	13.2
0.7	-0.0037	-0.0034	8.8
0.8	-0.0027	-0.0028	3.6
0.9	-0.0015	-0.0019	21.0
1.0	0.0000	0.0000	0.0

Average Error = 16.4

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).

Table XII

Predicted Versus Experimental Excess Thermal Conductivity

for the Methyl Ethyl Ketone-Chloroform System

Mole Fraction Chloroform	Predicted Excess Thermal Conductivity	Experimental Excess Thermal Conductivity	Percent Error
0.0	0.0000	0.0000	0.00
0.1	-0.0022	-0.0027	18.5
0.2	-0.0041	-0.0048	14.6
0.3	-0.0057	-0.0062	8.1
0.4	-0.0069	-0.0070	1.4
0.5	-0.0076	-0.0074	2.7
0.6	-0.0077	-0.0075	2.7
0.7	-0.0070	-0.0070	0.0
0.8	-0.0056	-0.0057	1.7
0.9	-0.0033	-0.0033	0.0
1.0	0.0000	0.0000	0.00

Average Error = 5.5

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).

Table XIII

Predicted Versus Experimental Excess Thermal Conductivity for the Acetone-Chloroform System

Mole Fraction Chloroform	Predicted Excess Thermal Conductivity	Experimental Excess Thermal Conductivity	Percent Error
0.0	0.0000	0.0000	00.0
0.1	-0.0020	-0.0030	26.6
0.2	-0.0040	-0.0056	23.2
0.3	-0.0058	-0.0073	15.1
0.4	-0.0072	-0.0083	7.2
0.5	-0.0081	-0.0086	0.0
0.6	-0.0084	-0.0084	6.0
0.7	-0.0079	-0.0074	13.5
0.8	-0.0064	-0.0059	15.3
0.9	-0.0038	-0.0036	13.9
1.0	0.0000	0.0000	00.0

Average Error = 13.6

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).

Table XIV

Predicted Versus Experimental Excess Thermal Conductivity

for the Benzene-Chloroform System

Mole Fraction Chloroform	Predicted Excess Thermal Conductivity	Experimental Excess Thermal Conductivity	Percent Error
0.0	0.0000	0.0000	0.00
0.1	-0.0013	-0.0018	27.8
0.2	-0.0024	-0.0034	29.4
0.3	-0.0033	-0.0045	26.5
0.4	-0.0040	-0.0053	24.6
0.5	-0.0043	-0.0053	20.4
0.6	-0.0044	-0.0050	12.0
0.7	-0.0040	-0.0045	11.1
0.8	-0.0031	-0.0038	18.4
0.9	-0.0018	-0.0023	21.8
1.0	0.0000	0.0000	0.00

Average Error = 21.3

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).

Table XV

Predicted Versus Experimental Excess Thermal Conductivity

for the Ethyl Ether-Chloroform System

Mole Fraction Chloroform	Predicted Excess Thermal Conductivity	Experimental Excess Thermal Conductivity	Percent Error
0.0	0.0000	0.0000	0.00
0.1	-0.0022	-0.0021	4.8
0.2	-0.0040	-0.0039	2.5
0.3	-0.0054	-0.0054	0.0
0.4	-0.0064	-0.0065	1.5
0.5	-0.0069	-0.0076	9.2
0.6	-0.0068	-0.0078	12.8
0.7	-0.0062	-0.0062	0.0
0.8	-0.0048	-0.0045	6.7
0.9	-0.0028	-0.0024	16.7
1.0	0.0000	0.0000	0.0

Average Error = 6.0

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).

Table XVI

Predicted Versus Experimental Excess Thermal Conductivity for the Toluene-Chloroform System

Mole Fraction Chloroform	Predicted Excess Thermal Conductivity	Experimental Excess Thermal Conductivity	Percent Error
0.0	0.0000	0.0000	00.0
0.1	-0.0021	-0.0017	23.6
0.2	-0.0038	-0.0032	18.8
0.3	-0.0051	-0.0042	21.4
0.4	-0.0059	-0.0053	11.3
0.5	-0.0063	-0.0060	5.0
0.6	-0.0062	-0.0062	0.0
0.7	-0.0055	-0.0059	6.8
0.8	-0.0043	-0.0049	12.2
0.9	-0.0024	-0.0031	22.6
1.0	0.0000	0.0000	00.0

Average Error = 13.5

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).

Table XVII

Predicted Versus Experimental Excess Thermal Conductivity

for the Diethyl Ketone-Chloroform System

Mole Fraction Chloroform	Predicted Excess Thermal Conductivity	Experimental Excess Thermal Conductivity	Percent Error
0.0	0.0000	0.0000	0.00
0.1	-0.0015	-0.0021	28.6
0.2	-0.0028	-0.0033	15.2
0.3	-0.0038	-0.0041	7.3
0.4	-0.0045	-0.0045	0.0
0.5	-0.0048	-0.0046	4.3
0.6	-0.0048	-0.0042	14.3
0.7	-0.0043	-0.0036	19.5
0.8	-0.0034	-0.0027	26.0
0.9	-0.0020	-0.0015	33.3
1.0	0.0000	0.0000	0.0

Average Error = 16.5

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).

Table XVIII

Predicted Versus Experimental Excess Thermal Conductivity

for the 1,2 dichloroethane-Methyl Ethyl Ketone System

Mole Fraction 1,2 dichloroethane	Predicted Excess Thermal Conductivity	Experimental Excess Thermal Conductivity	Percent Error
0.0	0.0000	0.0000	0.00
0.1	-0.0008	-0.0012	33.3
0.2	-0.0014	-0.0022	36.4
0.3	-0.0020	-0.0027	26.0
0.4	-0.0023	-0.0031	25.8
0.5	-0.0025	-0.0032	21.8
0.6	-0.0025	-0.0032	21.8
0.7	-0.0022	-0.0028	21.4
0.8	-0.0018	-0.0022	18.2
0.9	-0.0010	-0.0013	23.0
1.0	0.0000	0.0000	0.0

Average Error = 25.4

Thermal conductivity has units of BTU/(HR)(Ft)(^{o}F).

Table XIX

Predicted Versus Experimental Excess Thermal Conductivity

for the Chloroform-Methyl Isobutyl Ketone System

Mole Fraction Chloroform	Predicted Excess Thermal Conductivity	Experimental Excess Thermal Conductivity	Percent Error
0.0	0.0000	0.0000	0.0
0.1	-0.0011	-0.0009	22.2
0.2	-0.0020	-0.0016	25.0
0.3	-0.0026	-0.0023	13.0
0.4	-0.0030	-0.0027	11.1
0.5	-0.0032	-0.0030	6.6
0.6	-0.0030	-0.0032	6.6
0.7	-0.0027	-0.0032	15.6
0.8	-0.0020	-0.0032	37.5
0.9	-0.0011	-0.0023	52.0
1.0	0.0000	0.0000	0.0

Average Error = 21.0

Thermal conductivity has units of BTU/(HR)(FT)(^{o}F).

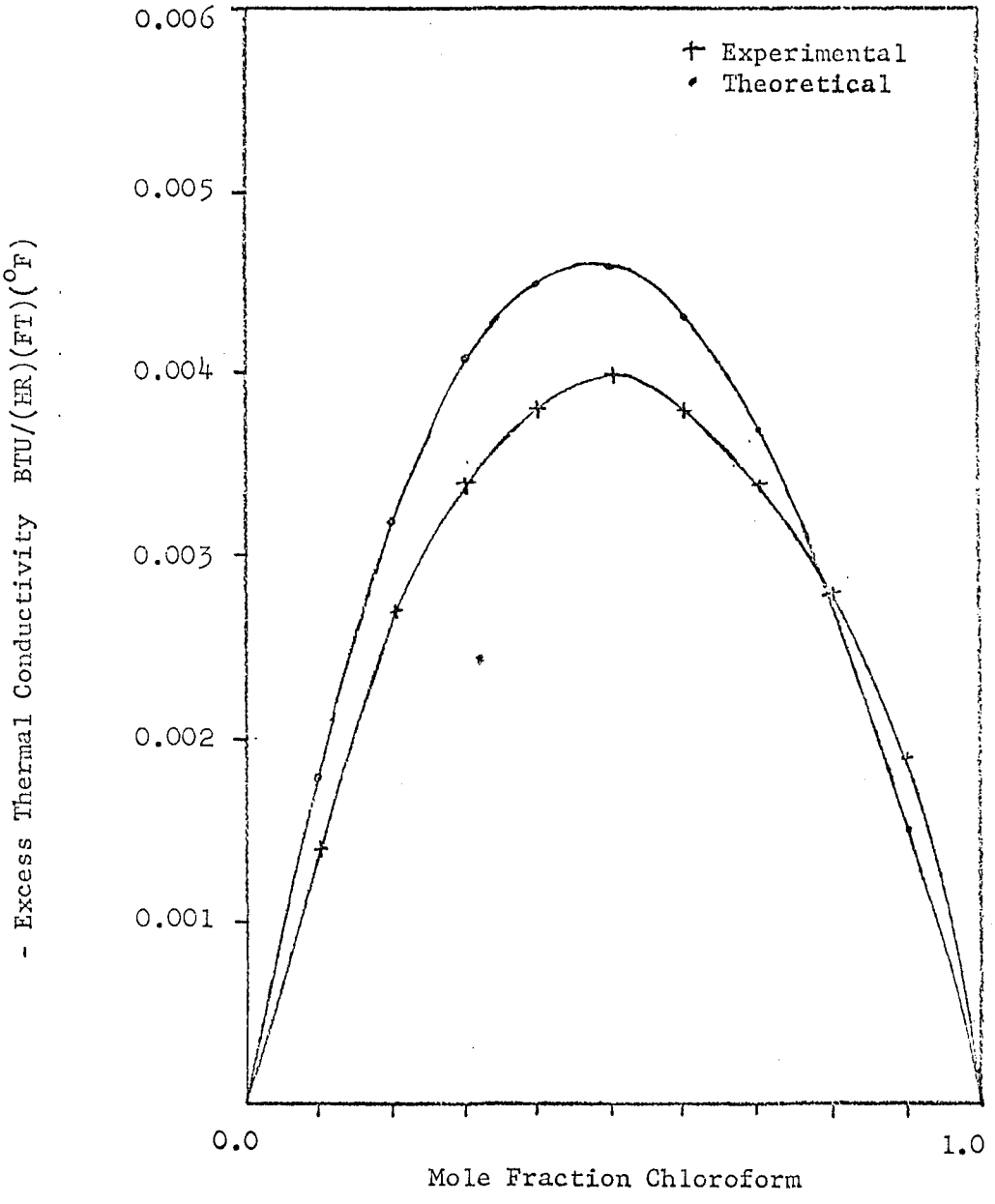


Fig. 15 Excess Thermal Conductivity versus Mole Fraction for the Chloroform-Isopropyl Ether System

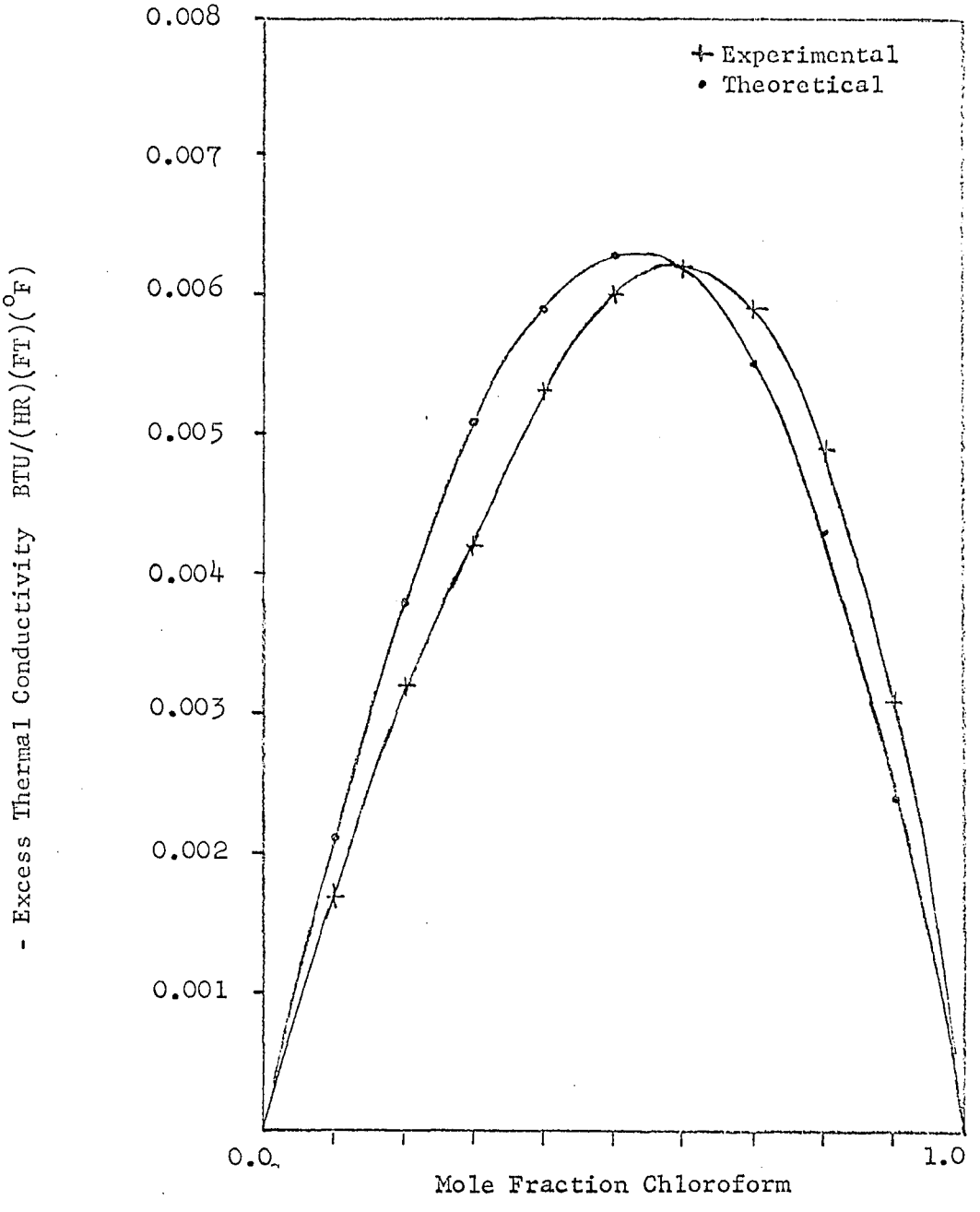


Fig. 16 Excess Thermal Conductivity versus Mole Fraction for the Toluene-Chloroform System

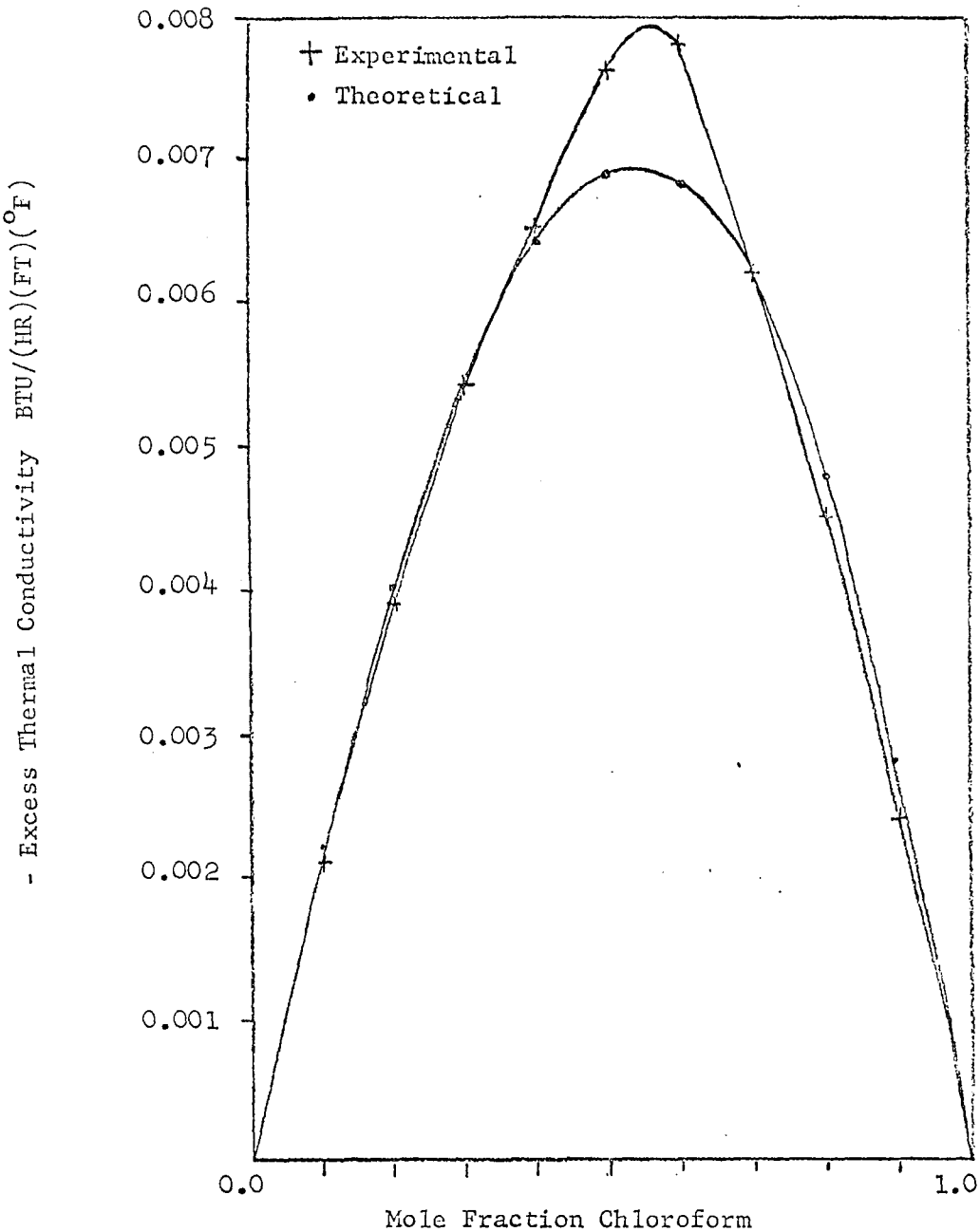


Fig. 17 Excess Thermal Conductivity versus Mole Fraction for the Chloroform-Ethyl Ether System

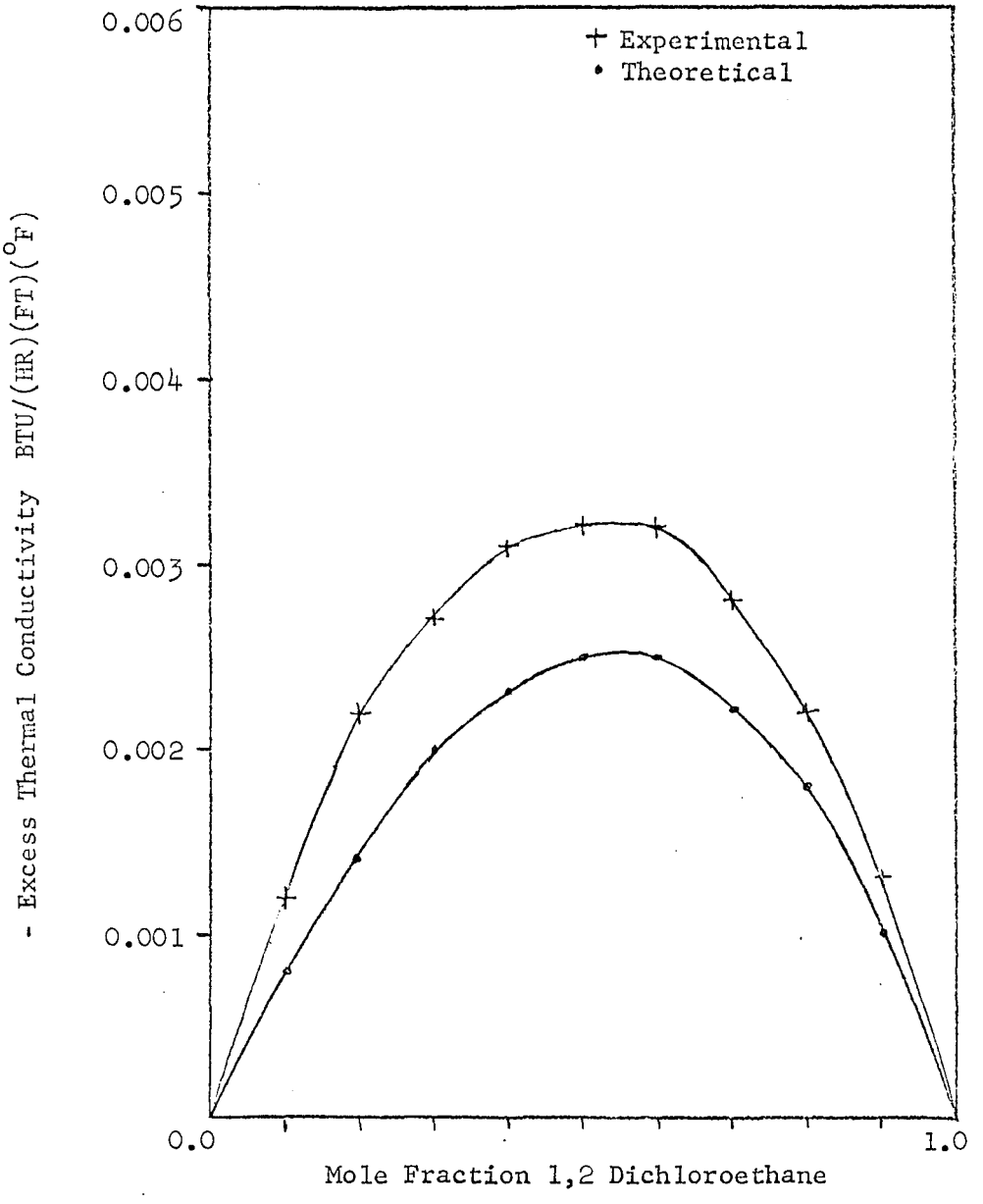


Fig. 18 Excess Thermal Conductivity versus Mole Fraction for the Methyl Ethyl Ketone - 1,2 Dichloroethane System

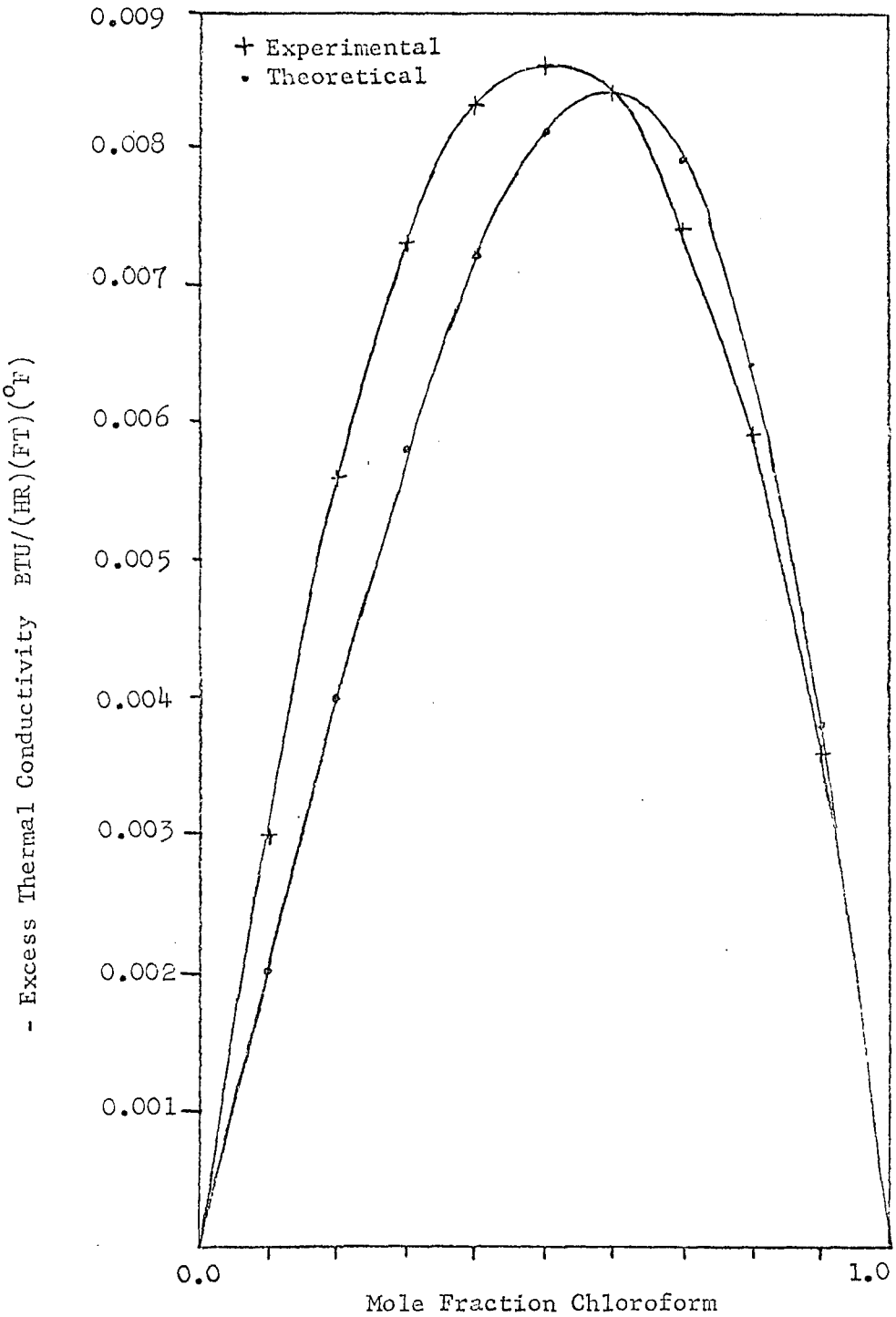


Fig. 19 Excess Thermal Conductivity versus Mole Fraction for the Acetone-Chloroform System

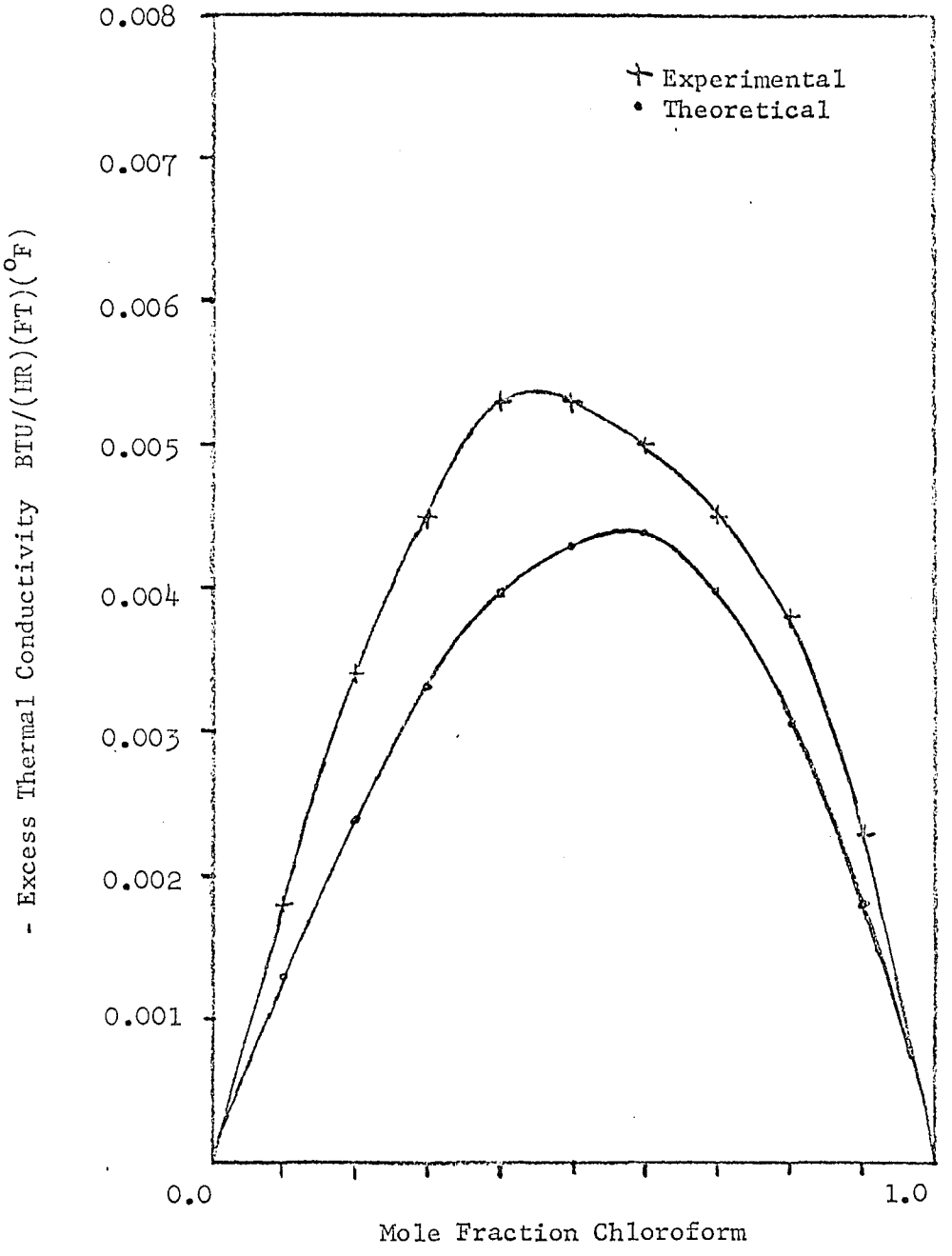


Fig. 20 Excess Thermal Conductivity versus Mole Fraction for the Chloroform-Benzene System

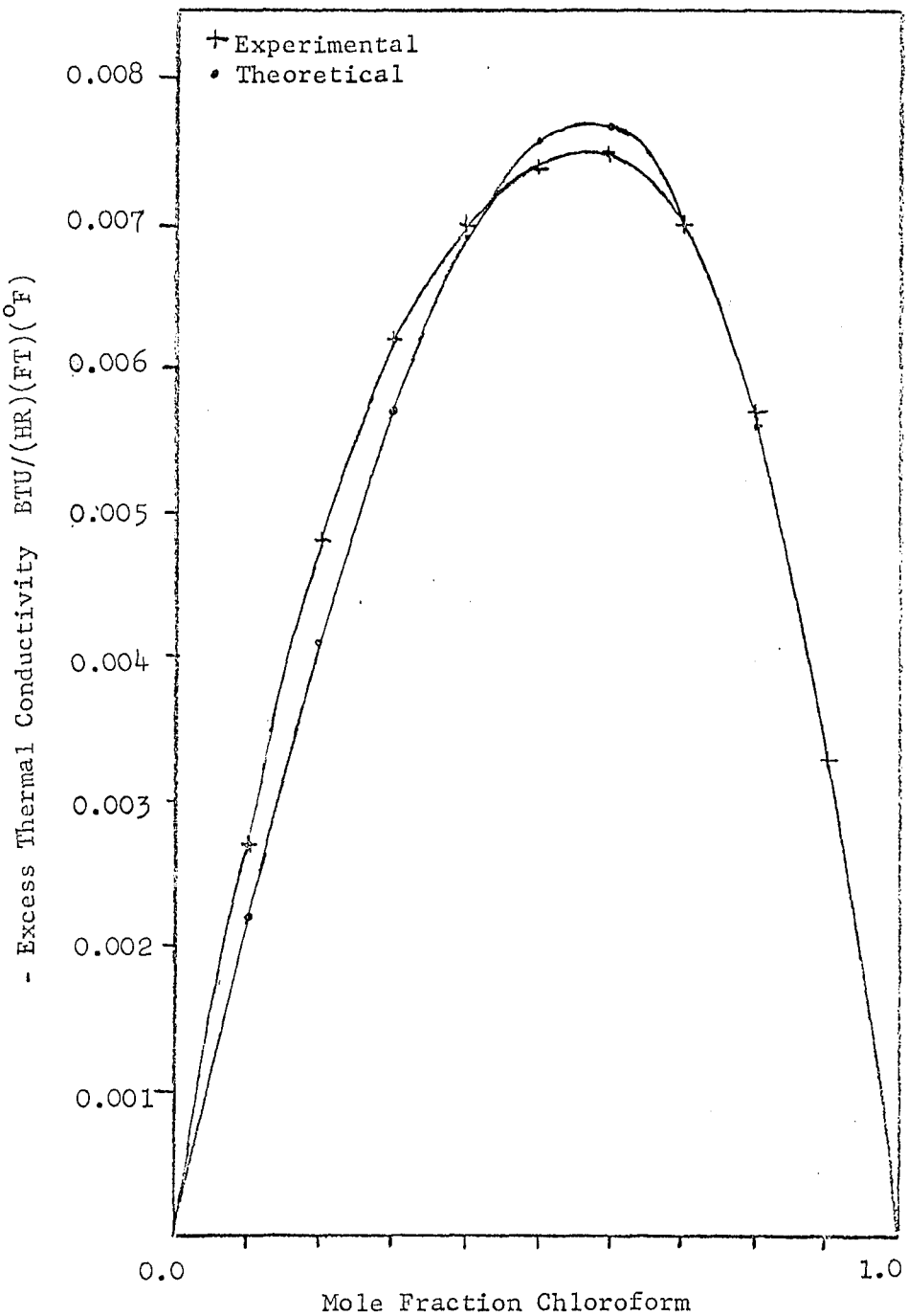


Fig. 21 Excess Thermal Conductivity versus Mole Fraction for the Methyl Ethyl Ketone-Chloroform System

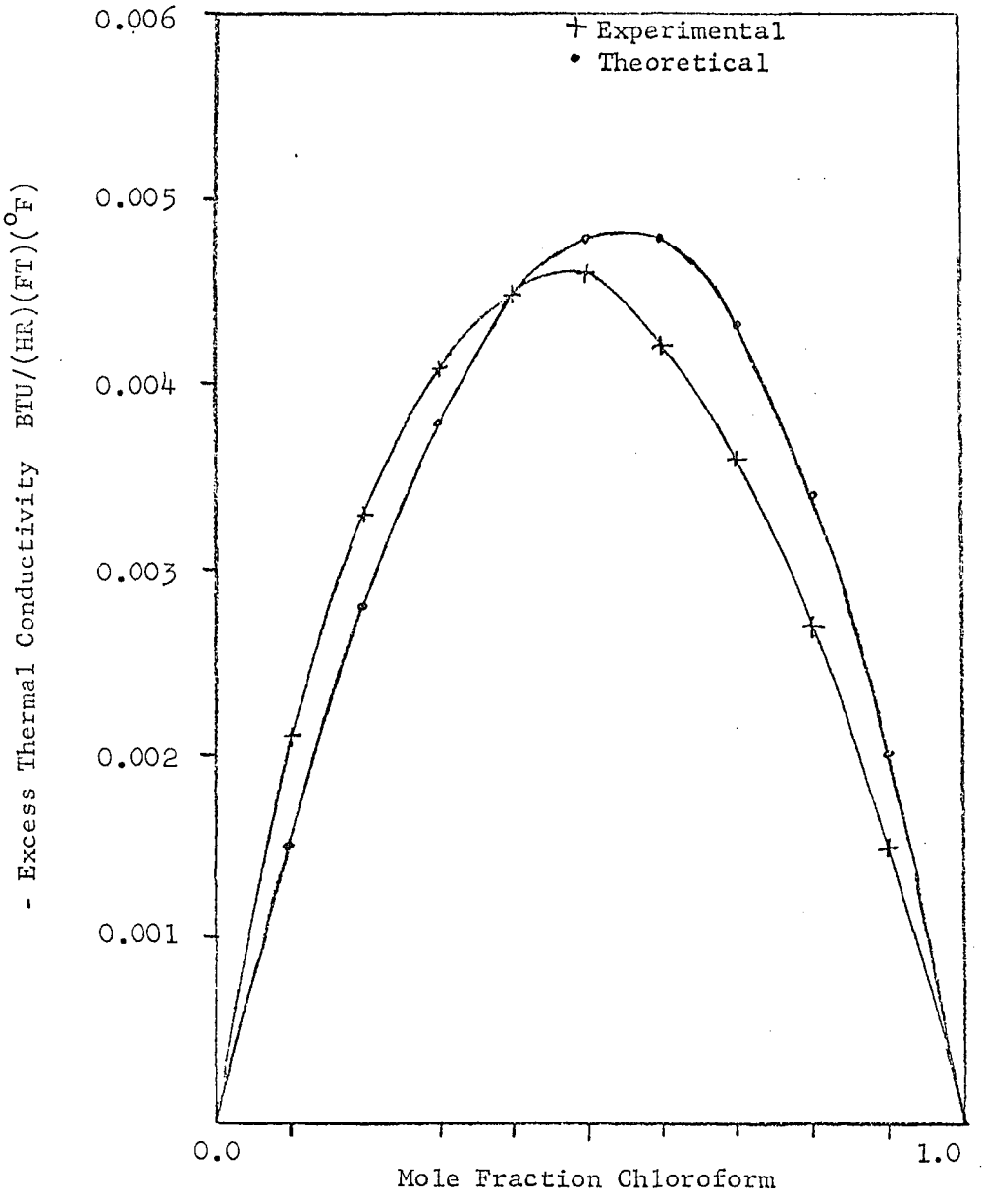


Fig. 22 Excess Thermal Conductivity versus Mole Fraction for the Chloroform-Diethyl Ketone System

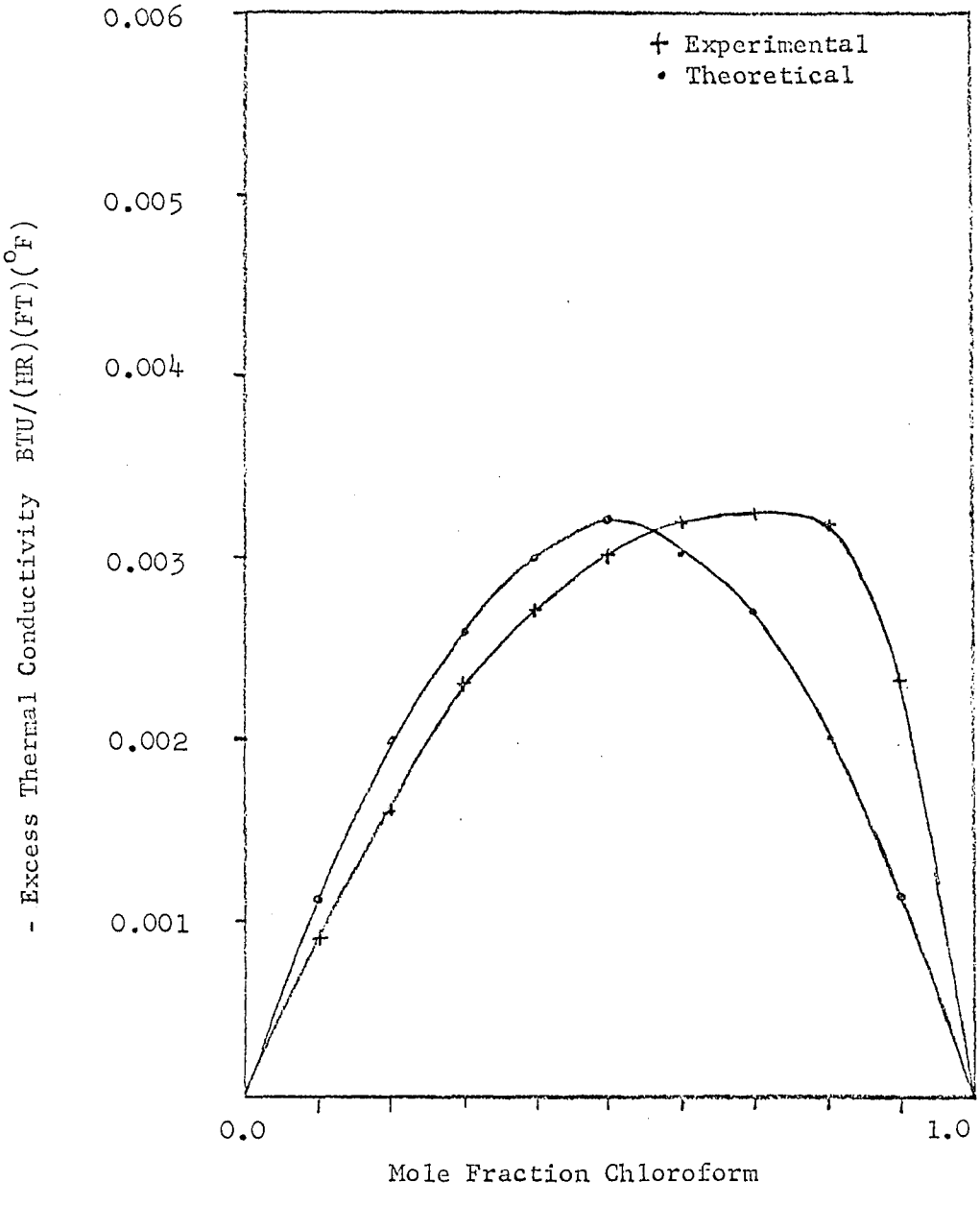


Fig. 23 Excess Thermal Conductivity versus Mole Fraction for the Chloroform-Methyl Isobutyl Ketone System

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CHAPTER 7
CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

As a result of this work, it is possible to calculate the excess thermal conductivity for binary solutions that form bimolecular hydrogen bonded complexes from the pure components. The major difficulty involved is obtaining enough data to use the equation developed, particularly an equilibrium constant for the hydrogen bond equilibria. For the systems studied, the calculated excess thermal conductivity agrees with the experimental excess thermal conductivity within 25%.

In addition to the method of predicting the excess thermal conductivity, an equally valuable qualitative conclusion can also be drawn from the data. The data indicates that as the hydrogen bond equilibria is decreased due to steric hindrance, the excess thermal conductivity decreases also. This was found to hold for both the data collected in this work and the thermal conductivity data collected previously on alcohols dissolved in inert solvents. From this conclusion it is possible to place an upper bound on the excess thermal conductivity for a system where no data is available. For example, the data for the system n-propanol-cyclohexane, Barnette has reported an excess thermal conductivity of -0.0057 at 0.50 mole fraction. From the above considerations, one would not expect the

next highest alcohol, n-butanol dissolved in cyclohexane, to have an excess thermal conductivity greater than -0.0057.

B. Recommendations for Further Work

For binary mixtures of alcohols and either a Lewis acid or base there would be two equilibria - one between the alcohol molecules in the form of chains and the other between the alcohol and the Lewis acid or base. For sterically hindered alcohols such as tertiary butanol or phenol the alcohol probably consists mostly of monomers and the only equilibria that would be considered would be the bimolecular complex formed between the alcohol and the Lewis acid or base which could be checked with the method of predicting excess thermal conductivity developed in Chapter Three.

The method proposed for calculating the excess thermal conductivity and the previous work of Barnette dealing with alcohols dissolved in inert solvents indicates that additional data on heats of reaction and equilibrium constants for hydrogen bonded systems are needed. This data can be obtained by use of an infrared spectrophotometer . Since a Beckman IR 8 infrared spectrophotometer is available and is probably suitable for this type of work, additional equipment requirements would be minimal.

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APPENDIX A
ERROR IN APPROXIMATING A FUNCTION WITH A HERMITE INTERPOLATING POLYNOMIAL[1]

Theorem

Given the value of a function $f(x)$ at n points and the value of the first derivative at n points, show that the error in approximating the function with a Hermite interpolating polynomial is given by $p^2(x)\frac{f^{(2n)}(\xi)}{(2n)!}$ where $p(x)$ is $(x-x_1)(x-x_2).....(x-x_n)$.

Since 2n conditions are given, then a Hermite interpolating polynomial of degree 2n-1 can be obtained.

Define the following function $F(x)$ as $F(x)\equiv f(x)-P_{2n-1}(x)-p^2(x)K$ such that at some arbitrary $\bar{x}$, $F(\bar{x})=0$. Since $p(x)$ was defined as $(x-x_1)(x-x_2).....(x-x_n)$, then $F(x_1)$, $F(x_2)$, ...$F(x_n)$, $F(\bar{x})=0$.

If $F(x)$ is differentiated, then:

$F'(x_1)=F'(x_2)=.....F'(x_n)=0$ since $f'(x)=p'_{2n-1}(x)$ at $x=x_1,x_2,\ ....x_n$.

In addition, Rolle's theorem states that if a function is continuous over the interval $[a,b]$ and differentiable in (a,b) and if $f(a) = f(b) = 0$, then there exists a point ξ in (a,b) such that $f'(\xi) = 0$.

By applying Rolle's theorem to the function $F'(x)$, there are 2n points where $F'(x)$ is zero. Applying Rolle's theorem to $F''(x)$, there are 2n-1 points where $F''(x)$ is zero. Continuing, it can be shown that at some point $F^{2n}(\xi) = 0$.

Since $F^{2n}(x) = f^{2n}(x) - (2n)!K$, then $F^{2n}(\xi) = f^{2n}(\xi) - (2n)!K$ or $K = \frac{f^{2n}(\xi)}{(2n)!}$.

The error in using a Hermite interpolating polynomial to approximate a function is given by $[(x-x_1)(x-x_2)....(x-x)_n]^2 \frac{f^{2n}(\xi)}{(2n)!}$.

Thus, if the function and its derivative are known at 2 points x_1 and x_2, then the error term is $(x-x_1)(x-x_2) \frac{f^4(\xi)}{4!}$. If it is known that the function being approximated is of order three, then $f^4(x)$ is zero and $f(x) = P_3(x)$ and there is no error encountered in using a Hermite interpolating polynomial.

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APPENDIX B
VIBRATIONAL FREQUENCY FOR A LINEAR HARMONIC OSCILLATOR[1]

The potential energy of a molecule displaced from its equilibrium site will be taken as being proportional to the square of the displacement:

$$V = \tfrac{1}{2} f z^2 .$$

This is a form of Hooke's Law.

The force at any instant is:

$$Y = -\frac{dV}{dz} = -fz .$$

From Newton's Second Law of Motion: $m \frac{d^2z}{dt^2} = -fz.$

This differential equation has the general solution:

$$z = C_1 \cos \left[\left(\frac{f}{m}\right)^{\frac{1}{2}} t + C_2 \right]$$

where C_1 and C_2 are constants. C_1 is the amplitude and C_2 is the initial phase angle. Let $\left(\frac{f}{m}\right)^{\frac{1}{2}} t + C_2 = \theta$

$$\cos \theta = \cos (2\pi + \theta)$$

The motion repeats itself when $2\pi = \left(\frac{f}{m}\right)^{\frac{1}{2}} t$. Let the time required for the motion to repeat itself to be T.

$$\therefore \left(\frac{f}{m}\right)^{\frac{1}{2}} T = 2\pi$$

Since the frequency is the reciprocal of the period: $\nu = \frac{1}{T}$.

$$\nu = \frac{(\frac{f}{m})^{\frac{1}{2}}}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{f}{m}}$$

For two species i, j, if $f_i \cong f_j$, then

$$\frac{\nu_i}{\nu_j} = \sqrt{\frac{M_j}{M_i}} .$$

APPENDIX B REFERENCES

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APPENDIX C
FREQUENCY RATIO FOR TWO SIMILAR MOLECULAR SPECIES BASED ON A RIGID SPHERE MOLECULAR INTERACTION

The Maxwell-Boltzmann velocity distribution[1] states the fraction of molecules with velocities between v and v + dv is:

$$\frac{4\pi e^{-mv^2/2KT}\, m^3 v^3 dv}{(2\pi m K T)^{\frac{3}{2}}} \tag{C-1}$$

where m is the mass of the molecule.

The mean velocity $\bar{v}$ can be defined as:

$$\bar{v} = \frac{\int_0^\infty f(v)v\,dv}{\int_0^\infty f(v)\,dv} \tag{C-2}$$

where f(v) is a velocity distribution function defined such that f(v)dv is the fraction of molecules with velocities between v and v + dv. Substituting the Maxwell-Boltzmann distribution function into equation (B-2) results in:

$$\bar{v} = \frac{\left(\frac{2KT}{m}\right)^{\frac{1}{2}} \int_0^\infty e^{-A^2} A^3\, dA}{\int_0^\infty e^{-A^2} A^2\, dA} \tag{C-3}$$

where the substitution $A = \left(\frac{m}{2KT}\right)^{\frac{1}{2}} v$ has been made.

Equation (B-3) can be integrated by making use of:[2]

$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4a} \sqrt{\frac{\pi}{a}}$$

and

$$\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2} \quad .$$

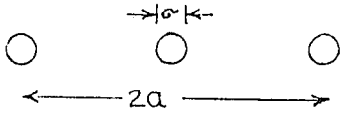
The result is $\bar{v} = \sqrt{\frac{8kT}{\pi m}}$.

For a hard sphere molecular interaction:

$u(r) - u(o) = 0 \qquad a - \sigma > r$

$u(r) - u(o) = \infty \qquad a - \sigma < r$ where u is potential energy, r is the distance between center, a the equilibrium distance between centers, and σ is the sphere diameter.

Thus a molecule can be considered to vibrate between 2 other molecules that are a distance of 2a apart:



The frequency of vibration can be thought of as:

$$\nu = \frac{\text{velocity}}{\text{wavelength}} \quad .$$

Since the wavelength is the distance traversed in a complete cycle or $4(a-\sigma)$, then

$$\nu = \sqrt{\frac{8KT}{\pi m}} \quad \frac{1}{4(a-\sigma).}$$

For 2 molecular species i,j that are similar enough to assume that $(a_i - \sigma_i) = (a_j - \sigma_j)$, then

$$\frac{\nu_i}{\nu_j} = \sqrt{\frac{m_j}{m_i}} \quad .$$

APPENDIX C REFERENCES

[1]T. L. Hill, Introduction to Statistical Thermodynamics, (Reading, Massachusetts: Addison-Wesley, 1960), p. 123.

[2]R. S. Burington, Handbook of Mathematical Tables and Formulas, (New York: McGraw-Hill, 1965), p. 105.

APPENDIX D
THERMAL CONDUCTIVITY RATIOS FOR RIGID MOLECULES WITH SIMILAR SIZES AND SHAPES

Equation (3-37) should be applicable to the prediction of the ratio of thermal conductivities of pure liquids whose molecules are approximately rigid and which have similar shapes and sizes. For example, molecular species such as benzene and toluene which have similar sizes and shapes, the binding constants should be equal and the frequency ratios should be inversely proportional to the square root of molecular weight. The distance between centers can be obtained from density and molecular weight data. The result is:

$$\frac{k_a}{k_b} = \sqrt{\frac{M_b}{M_a}} \sqrt[3]{\frac{M_b}{M_a}\frac{\rho_a}{\rho_b}} .$$

A test of the above relation for similar substances is shown below:

Substances	$\frac{k_a}{k_b}$	$\sqrt{\frac{M_b}{M_a}} \sqrt[3]{\frac{M_b}{M_a}\frac{\rho_a}{\rho_b}}$	Source of Thermal Conductivity Data
Benzene Toluene*	0.919	0.872	1
Methyl Ethyl Ketone Methyl Isobutyl Ketone*	1.178	1.248	Author
Ethyl Ether* Isopropyl Ether	1.310	1.303	Ethyl Ether-2 Isopropyl Ether-Author
Cyclohexane* Methyl Cyclohexane	1.142	1.140	1
Chlorobenzene* Bromobenzene	1.15	1.195	1
Iodobenzene* Bromobenzene	0.903	0.872	1
Chlorobenzene* Iodobenzene	1.268	1.385	1

*Refers to component a

APPENDIX D REFERENCES

[1]N. V. Tsederberg, Thermal Conductivity of Gases and Liquids, (Cambridge, Massachusetts: M.I.T. Press, Massachusetts Institute of Technology, 1965), p. 199.

[2]L. P. Fillippov and N. S. Novoselova, "The Thermal Conductivity of Solutions of Normal Mixtures," Vestnik Moskovskogo Universiteta, Seriya Fiziko-Matenatecheskikhi Estestvennykk Nauk, No. 3, X (1955), p. 37.

APPENDIX E
EVALUATION OF THE EQUILIBRIUM CONSTANT FROM ACTIVITY[1] COEFFICIENT DATA

The formation of the hydrogen bonded complex AB from the acid A and the base B will be written as $A + B \rightleftarrows AB$. The equilibrium mixture of A,B, and AB will be assumed to be ideal. The chemical potential of component A written in terms of the actual mole fraction of A is:

$$\mu_A = \mu_A''(T,P) + RT\ln x_A \quad .$$

The chemical potential of component A can also be written in terms of the apparent mole fraction of A and an activity coefficient γ_A:

$$\mu_A = \mu_A'(T,P) + RT\ln \gamma_A x_A^{\,o}$$

Equating these two results:

$$\mu_A'(T,P) + RT \ln \gamma_A x_A^{\,o} = \mu_A''(T,P) + RT \ln x_A \quad .$$

When $x_A = 1$, the activity coefficient γ_A equals unity and hence $\mu_A'(T,P) = \mu_A''(T,P)$. Therefore:

$$RT \ln \gamma_A x_A^{\,o} = RT \ln x_A$$

Hence the activity coefficient is the ratio of the actual mole fraction to apparent mole fraction:

$$\gamma_A = \frac{x_A}{x_A^{\,o}} \quad .$$

An equilibrium constant K will be defined as:

$$K = \frac{x_{AB}}{x_A x_B} .$$

For each mole of complex formed, a mole of acid or base is consumed:

$$n_A = n_A^o - n_{AB}$$

$$n_B = n_B^o - n_{AB}$$

where n_{AB} is the number of moles of complex formed, n_A^o and n_B^o are respectively the moles of acid and base initially present, and n_A and n_B are respectively the number of moles of acid and base present at equilibrium.

From the preceding, the mole fractions of each component can be expressed as:

$$x_A = \frac{n_A^o - n_{AB}}{n_A^o + n_B^o - n_{AB}}$$

$$x_B = \frac{n_B^o - n_{AB}}{n_A^o + n_B^o - n_{AB}}$$

$$x_{AB} = \frac{n_{AB}}{n_A^o + n_B^o - n_{AB}}$$

Making use of the above and equation (-3), the equilibrium constant can be expressed as:

$$K = \frac{1 - \gamma_A}{\gamma_A(1-2x_A^o + \gamma_A x_A^{o\,2})} .$$

APPENDIX E REFERENCES

[1] I. Prigogine, Chemical Thermodynamics, (London: Longmans, Green, and Co., 1954), p.

APPENDIX F
NOMENCLATURE

a	Distance between centers of molecules
c	Total molar concentration
D_{im}	Mutual diffusion coefficient of component i in a mixture m
D^{o}_{32}	Mutual diffusion coefficient of component 3 in 2 infinitely dilute in 3
D^{o}_{31}	Mutual diffusion coefficient of component 3 in 1 infinitely dilute in 3
f	Hooke's law constant
$\bar{H}_i$	Partial molal enthalpy
K	Equilibrium constant
k_1	Thermal conductivity of component 1
k_2	Thermal conductivity of component 2
k_3	Thermal conductivity of component 3
k_f	Thermal conductivity without chemical reaction
k_s	Thermal conductivity of the solution
M	Molecular weight
N_i	Molar flux
R	Gas constant
U	Velocity of sound
V	Molar volume
x	Mole fraction
z	Distance

Greek Symbols

κ	Boltzmann's constant
ν	Frequency
ρ	density

APPENDIX G

THERMAL CONDUCTIVITY VALUES UNCORRECTED FOR TEMPERATURE

Table XXI

Experimental Thermal Conductivity Values for

Mixtures of Chloroform and Methyl Ethyl Ketone

Mole Fraction Chloroform	Temperature F	Solution Thermal Conductivity	Thermal Conductivity at 25°C
0.0000	87.42	0.0853	0.0870
0.2171	87.26	0.0754	0.0770
0.4261	87.26	0.0703	0.0719
0.6256	87.27	0.0680	0.0696
0.8154	87.19	0.0640	0.0654
1.0000	87.24	0.0659	0.0671

Thermal conductivity has units of BTU/(HR)(FT)(°F).

Table XXII

Experimental Thermal Conductivity Values for

Mixtures of Chloroform and Toluene

Mole Fraction Chloroform	Temperature F	Solution Thermal Conductivity	Thermal Conductivity at 25°C
0.0000	87.40	0.0777	0.0787
0.2368	87.33	0.0718	0.0728
0.4451	87.31	0.0665	0.0676
0.6624	87.24	0.0637	0.0649
1.0000	87.24	0.0659	0.0671

Thermal conductivity has units of BTU/(HR)(FT)(°F).

Table XXIII

Experimental Thermal Conductivity Values for
Mixtues of Chloroform and Methyl Isobutyl Ketone

Mole Fraction Chloroform	Temperature F	Solution Thermal Conductivity	Thermal Conductivity at 25°C
0.0000	87.33	0.0730	0.0739
0.2656	87.30	0.0689	0.0699
0.4972	87.35	0.0667	0.0679
0.6840	87.18	0.0650	0.0662
0.6905	87.24	0.0643	0.0656
0.8475	87.18	0.0640	0.0653
1.0000	87.24	0.0659	0.0671

Thermal conductivity has units of BTU/(HR)(FT)(°F).

Table XXIV

Experimental Thermal Conductivity Values for Mixtures of Chloroform and Diethyl Ketone

Mole Fraction Chloroform	Temperature F	Solution Thermal Conductivity	Thermal Conductivity at 25°C
0.0000	87.23	0.0826	0.0832
0.2414	87.05	0.0747	0.0755
0.4566	87.07	0.0707	0.0717
0.6572	87.20	0.0672	0.0684
0.8478	87.21	0.0664	0.0677
1.0000	87.24	0.0659	0.0671

Thermal conductivity has units of BTU/(HR)(FT)(°F).

Table XXV

Experimental Thermal Conductivity Values for

Mixtures of 1,2 dichloroethane and Methyl Ethyl Ketone

Mole Fraction 1,2 dichloroethane	Temperature F	Solution Thermal Conductivity	Thermal Conductivity at 25°C
0.0000	87.42	0.0853	0.0870
0.2022	87.35	0.0815	0.0830
0.4274	87.38	0.0803	0.0816
0.6357	87.34	0.0772	0.0783
0.8305	87.42	0.0767	0.0777
1.0000	87.29	0.0773	0.0781

Thermal conductivity has units of BTU/(HR)(FT)(°F).

Table XXVI

Experimental Thermal Conductivity Values for

Mixtures of Chloroform and Isopropyl Ether

Mole Fraction Chloroform	Temperature F	Solution Thermal Conductivity	Thermal Conductivity at 25°C
0.0000	87.10	0.0606	0.0608
0.2963	87.02	0.0588	0.0594
0.5360	87.18	0.0600	0.0606
0.8772	87.22	0.0625	0.0638
1.0000	87.24	0.0659	0.0671

Thermal conductivity has units of BTU/(HR)(FT)(°F).

AUTOBIOGRAPHY

The author was born February 27, 1939, in Picher, Oklahoma, the oldest of three sons of Clayton H. and Mildred Phillips Kerr. He attended the public schools of Miami, Oklahoma and graduated from Miami High School in 1957.

In September, 1957 the author enrolled in Northeastern A and M College in Miami, Oklahoma. In June, 1958 the author enrolled at the University of Oklahoma at Norman, Oklahoma and subsequently graduated in June, 1961 with a Bachelor of Science Degree in Chemical Engineering. From June 1961 until February, 1965 the author was employed by Humble Oil and Refining Company in Baton Rouge, Louisiana as a chemical engineer. In February, 1965 the author started graduate school in the Department of Chemical Engineering at Louisiana State University in Baton Rouge, Louisiana and was simultaneously appointed for one semester to fill a temporary vacancy as an undergraduate instructor of chemical engineering. In August, 1966 the author received a Master of Science Degree in Chemical Engineering. The author is presently a candidate for the degree of Doctor of Philosophy in Chemical Engineering.

Upon graduation, the author plans to join the Department of Chemical Engineering at Tennessee Technological University in Cookeville, Tennessee as an assistant professor of chemical engineering.

EXAMINATION AND THESIS REPORT

Candidate: Clayton Phillips Kerr

Major Field: Chemical Engineering

Title of Thesis: A Method of Predicting the Thermal Conductivity of Some Hydrogen Bonded Binary Solutions That Form Bimolecular Complexes

Approved:

Jesse Coates
Major Professor and Chairman

R D Anderson
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EXAMINING COMMITTEE:

L L Saunders

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Date of Examination:

July 18, 1968